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(71)Applicant : SEIKO EPSON CORP
ORIENT CHEM IND LTD

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(72)Inventor : ITO HIROSHI
MOMOSE MASAYUKI
HAYASHI HIROKO
ITO SOUSHI

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(54) AQUEOUS PIGMENT DISPERSION, AQUEOUS INK COMPOSITION, AND RECORDING BY USING THE INK COMPOSITION

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain an aqueous pigment dispersion capable of providing high printing density, and further to provide an ink composition.

SOLUTION: This aqueous pigment dispersion consists essentially of water and a surface-modified carbon black, and the surface-modified carbon black is the one having 0.3-2.5 ratio of a specific surface area (m²/g) to a DBP oil absorption (ml/100 g), and a hydrophilic functional group introduced on the surface. As a result, the carbon black can be dispersed and/or dissolved in the water without using a dispersing agent.

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CLAIMS

[Claim(s)]

[Claim 1] Watercolor pigment dispersion liquid distribution and/or whose dissolution are watercolor pigment dispersion liquid which come to contain water and surface treatment carbon black at least, and the ratios of specific surface area (m^2/g) / DBP oil absorption ($\text{ml} / 100\text{g}$) is [this surface treatment carbon black] 0.3–2.5, a hydrophilic functional group is introduced into the front face, consequently are enabled without a dispersant at water.

[Claim 2] Watercolor pigment dispersion liquid according to claim 1 whose ratios of specific surface area (m^2/g) / DBP oil absorption ($\text{ml} / 100\text{g}$) of said surface treatment carbon black are 0.3–1.75.

[Claim 3] Watercolor pigment dispersion liquid according to claim 1 or 2 said whose surface treatment carbon black is what has the hydrophilic functional group of 1.5 or more mmol/g .

[Claim 4] How to come to contain the process which wet oxidation of the carbon black whose ratios of specific surface area / DBP oil absorption it is the manufacture approach of the watercolor pigment dispersion liquid a publication, and are 0.3–2.5 is carried out [process] to any 1 term of claims 1–3 using the following ** halogen acid or its salt, and a hydrophilic functional group is introduced [process], and distributes and/or dissolves said carbon black without a dispersant in water.

[Claim 5] The water-color-ink constituent which comes to contain the watercolor pigment dispersion liquid of a publication in any 1 term of claims 1–3 at least.

[Claim 6] The ink constituent according to claim 5 which has permeability [as / whose penetration time of an ink constituent is less than 1 second] when the coverage of the ink constituent to a record medium is 1 mg/cm^2 .

[Claim 7] The water-color-ink constituent according to claim 5 or 6 whose surface tension of an ink constituent is less than 40 mN/m .

[Claim 8] A water-color-ink constituent given in any 1 term of claims 5–7 which come to contain the water-soluble organic solvent of a glycol butyl ether system further.

[Claim 9] A water-color-ink constituent given in any 1 term of claims 5–8 which come to contain the Nonion nature surfactant further.

[Claim 10] The water-color-ink constituent according to claim 9 whose Nonion nature surface active agent is an acetylene glycol system surface active agent.

[Claim 11] The record approach are the record approach of making an ink constituent adhering and printing to a record medium, and using a water-color-ink constituent given [as an ink constituent] in any 1 term of claims 5–10.

[Claim 12] The ink jet record approach are the ink jet record approach of adhering the drop of an ink constituent to discharge and printing by making this drop adhering to a record medium, and using a water-color-ink constituent given [as an ink constituent] in any 1 term of claims 5–10.

[Claim 13] The record object in which record was performed by the record approach according to claim 11 or 12.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Background of the Invention] Field this invention of invention relates to the watercolor pigment dispersion liquid which come to contain the carbon black which carried out surface treatment, and the water-color-ink constituent which comes to contain these watercolor pigment dispersion liquid.

[0002] The water-soluble color has been used for the recording ink used for the writing implement and ink jet printer of the background technical conventional aquosity. On the other hand, in order to improve the image quality and endurance of a record object in recent years, a pigment like carbon black is used for the coloring agent. For example, the watercolor pigment ink which distributed carbon black with the surfactant or the macromolecule dispersant is indicated by JP,64-6074,A and JP,64-31881,A.

[0003] However, in these ink, in order to raise the printing concentration of a record object, when the ink content of a coloring agent was increased, in connection with it, ink viscosity might also increase rapidly. Moreover, in order to distribute carbon black stably in ink, the superfluous surfactant or the macromolecule dispersant was required, but since these existence caused gassing and an antifoam fall, in the case of the ink for ink jet record, it was observed especially that printing stability gets worse.

[0004] In order to solve these technical problems, the surface activity hydrogen more than a constant rate or its salt is introduced into carbon black, and even if there is neither a surface active agent nor a giant-molecule dispersant, the surface treatment carbon black dispersion liquid which a drainage system solvent can be made to distribute by the carbon black independent are indicated by JP,8-3498,A and JP,10-120958,A. Moreover, the approach of introducing a sulfone radical into carbon black is indicated by JP,10-110127,A. Furthermore, the ink jet ink containing above-mentioned surface treatment carbon black and glycol ether is proposed by JP,10-95941,A.

[0005]

[Summary of the Invention] this invention person etc. acquired knowledge that high printing of printing concentration can be realized and the ink constituent which can form a higher-definition record object is obtained by the surface treatment carbon black obtained by reforming a front face with the specific surface area / DBP oil absorption ratio of the specific range this time. This invention is based on this knowledge.

[0006] Therefore, this invention can carry out high printing of printing concentration, and sets offer of the watercolor pigment dispersion liquid which can form a higher-definition record object, and a water-color-ink constituent as the purpose.

[0007] And it is watercolor pigment dispersion liquid which come to contain water and surface treatment carbon black at least, and this surface treatment carbon black is [the ratios of specific surface area (m²/g) / DBP oil absorption (ml / 100g)] 0.3-2.5, a hydrophilic functional group is introduced into the front face, consequently distribution and/or the dissolution of the watercolor pigment dispersion liquid of this invention are enabled without a dispersant at water.

[0008] Moreover, the water-color-ink constituent of this invention comes to contain said

watercolor pigment dispersion liquid at least.

[0009]

[Detailed Description of the Invention] Coming [water and surface treatment carbon black] at least, when the ratio of specific surface area / DBP oil absorption is carbon black of 0.3–2.5 and, as for this surface treatment carbon black, introduces a hydrophilic functional group, reforming of that front face is carried out, consequently, as for the watercolor pigment dispersion liquid by watercolor pigment dispersion–liquid this invention, distribution and/or the dissolution of it are enabled without a dispersant at water.

[0010] A carbon black front face is reformed and a hydrophilic property is made to hold to carbon black itself by it in this invention by introducing a hydrophilic functional group into carbon black in large quantities. For this reason, it is thought that the carbon black by which surface treatment was carried out serves as particle diameter (preferably the minimum particle diameter) which can distribute this carbon black, and is underwater distributed without the assistance of a dispersant so that water soluble dye may dissolve in water by the single molecule. Although such surface treatment carbon black is usually called self–distributed carbon black, such carbon black is used for it in this invention.

[0011] An ink constituent can be prepared without a dispersant by using the watercolor pigment dispersion liquid by this invention. Consequently, even if it raises the concentration of carbon black, the viscosity of an ink constituent cannot change a lot and can make high–concentration carbon black exist in an ink constituent. Therefore, a high–concentration printing image is realizable. Furthermore, the watercolor pigment dispersion liquid by this invention are using the carbon black by which the specific surface treatment which is the ratio of specific surface area / DBP oil absorption was made, and have an advantage that the improvement of a remarkable image is achieved as compared with the carbon black with which are not satisfied of the requirements by this invention.

[0012] In this invention, “they are distribution and/or the dissolution without a dispersant to water” means the condition of existing stably with the particle diameter which can be distributed underwater, without carbon black using a dispersant. The particle diameter which can be distributed means the particle diameter to which a particle does not become small any more even if it increases distributed time amount.

[0013] In this invention, the ratio of specific surface area (m^2/g) and DBP oil absorption ($\text{ml} / 100\text{g}$) is carbon black of 0.3–2.5, and the carbon black of 0.3–1.75 has [the carbon black used in order to carry out surface treatment] the desirable ratio of specific surface area / DBP oil absorption.

[0014] In this invention, specific surface area (m^2/g) can make gas able to stick to carbon black, and it can ask for it by computing the surface area of carbon black from the molecule cross–sectional area in the amount of adsorption and adsorbed state (known as a nitrogen adsorption process). In addition, in this invention, when calling it the specific surface area of carbon black, the specific surface area based on the carbon black of which mode of surface treatment carbon black and the carbon black of surface non–reforming used as the raw material shall also be included. Moreover, it is presumed that the specific surface area of surface treatment carbon black and the specific surface area of the carbon black of surface non–reforming show a the same and almost equivalent value substantially.

[0015] Moreover, DBP oil absorption ($\text{ml} / 100\text{g}$) is a value expressed as an amount of dibutyl phthalate (DBP) absorbed by carbon black 100g, and is JIS. It can ask according to the measuring method specified to K6221. In addition, according to said measuring method, abb SOPUTO meter is used and the DBP absorbed amount per [for which it asked from 70% of the maximum torque when adding DBP to carbon black] 100g is calculated.

[0016] The color black FW18 which is carbon black by #20B and #40 grade; Degussa AG which is carbon black by Mitsubishi Chemical, Inc. as an example of the carbon black preferably used in this invention, the color black S170, and special black 250 grade; MONAKU 700 and MONAKU 880 which are carbon black by the KONDAKU tex SC which is carbon black by the Colombia carbon company, Rahaeng 1255 grade, and Cabot Corp., and elf tex 12 grade are mentioned.

[0017] The surface treatment carbon black in this invention can be obtained by introducing a

hydrophilic functional group into the above carbon black, and reforming a front face.

[0018] Here, it means combining hydrophilic functional groups, such as the carboxyl group "which introduces a hydrophilic functional group", a carbonyl group, hydroxyl, a sulfone radical, a phosphate group, and quaternary ammonium salt, and the salt of those with the front face of the carbon black which is a pigment through direct or an alkyl group, an alkyl ether radical, or an aryl group.

[0019] For example, the surface treatment carbon black in this invention can be obtained by making a pigment front face carry out the graft of the active species containing a functional group or a functional group by physical processing and chemical preparation of the vacuum plasma etc. Moreover, this surface treatment carbon black can also be obtained also by introducing a carboxyl group through a phenyl group oxidizing a pigment front face with an oxidizing agent underwater, and introducing hydrophilic functional groups, such as a carboxyl group and a sulfone radical, or by combining a p-amino-benzoic acid etc.

[0020] In the desirable mode of this invention, surface treatment carbon black oxidizes the carbon black front face of a pigment with an oxidizer underwater, and it comes to introduce a hydrophilic functional group into this front face.

[0021] In the still more desirable mode of this invention, surface treatment carbon black is 0.3–2.5, the ratio of specific surface area / DBP oil absorption carries out wet oxidation using the following ** halogen acid or its salt, and it comes to introduce a hydrophilic functional group into the front face. Here, as the following ** halogen acid or its salt, a hypochlorous-acid water solution, a sodium hypochlorite, potassium hypochlorite, a hypobromous acid water solution, hypobromous acid sodium, a hypobromous acid potassium, etc. are mentioned, for example. In these, the point of reactivity or cost to a sodium hypochlorite is desirable.

[0022] Therefore, according to this invention, it is the manufacture approach of the above mentioned watercolor pigment dispersion liquid, and wet oxidation of the carbon black whose ratios of specific surface area / DBP oil absorption are 0.3–2.5 is carried out using the following ** halogen acid or its salt, a hydrophilic functional group is introduced, and the approach of coming to contain the process which distributes and/or dissolves said carbon black without a dispersant in water is also offered.

[0023] In order to oxidize a pigment front face underwater, to introduce a hydrophilic functional group and to obtain surface treatment carbon black, the above carbon black and sodium hypochlorites are usually mixed in underwater, and a reaction is advanced preferably for 10 to 20 hours for 5 hours or more. As for carbon black, it is desirable in that case to make it react to coincidence, grinding [before making it react, grind, or]. As the grinding approach, carbon black may be performed with beads, such as glass, a zirconia, an alumina, stainless steel, or magnetism, by grinding by the ball mill, attritor, the colloid mill, or the sand mill. Moreover, when it is that which carbon black is easy to be cracked, a rotating type homogenizer or an ultrasonic homogenizer may grind carbon black.

[0024] After grinding and oxidizing carbon black, a bead and a big and rough particle are separated and removed from the obtained liquid, subsequently ultrafiltration for removing the by-product and the superfluous ion of an oxidizer etc. is refined, and watercolor pigment dispersion liquid are obtained. Moreover, if needed, the classification by the filtration using concentration, a metal filter, a membrane filter, etc. in a demarcation membrane etc. or centrifugal separation etc. may be performed, and the hydroxide or amine of an alkali-metal salt may neutralize.

[0025] the watercolor pigment dispersion liquid by this invention — if it is, the amount of hydrophilic functional groups in surface treatment carbon black after carrying out wet oxidation is 1.5 or more mmol/g preferably. Such by being a value, the amount of hydrophilic functional groups becomes possible [distributing or dissolving without a dispersant in water]. The amounts of hydrophilic functional groups, such as a carboxyl group in the surface treatment carbon black generated by oxidation treatment, a carbonyl group, or hydroxyl, can be judged by the vacuum cracked gas method which measures the volatile matter of general carbon black. in addition, said vacuum cracked gas method — the Chemical Society of Japan — it is the approach of a page [of volume / 88th / three No. (1967) / 69–74th] publication, and they are specifically the following approaches.

[0026] That is, the amount of hydrophilic functional groups in surface treatment carbon black is measured by using the vacuum thermal-analysis equipment which comes to have the electric furnace and gas chromatograph like drawing 1. Here, by a gas chromatograph considering as the thing of a middle cel type, a column fills up the first step with silica gel, it fills up the second step with molecular-sieve 13X, respectively, and an argon is used as carrier gas. Weighing capacity of the carbon black 0.1–0.5g which is a sample is carried out, it puts into a quartz tube and an electric furnace is loaded, and in order to remove adsorption moisture and air as pretreatment, evacuation is carried out at 120 degrees C for 2 hours. Next, the temperature controller of an electric furnace is set as 200 degrees C, it maintains for 1 hour, uptake of the generating gas in the meantime is carried out, it applies to a gas chromatograph, and a presentation is analyzed. And immediately, uptake of the generating gas of 1 hour which sets up and follows 300 degrees C is carried out, it is analyzed, one by one, uptake of the generating gas of 1 hour each in 400 degrees C, 500 degrees C, 600 degrees C, 700 degrees C, 800 degrees C, 900 degrees C, and 1000 degrees C is carried out, and the presentation is analyzed henceforth. In addition, generating gas is mainly a carbon monoxide and a carbon dioxide: thus, each acquired temperature conditions — the amount of hydrophilic functional groups in surface treatment carbon black is computed from the data of the presentation in the generating gas to kick.

[0027] In the watercolor pigment dispersion liquid by this invention, water is the main solvent. Pure water, such as ion exchange water, ultrafiltration water, Milli Q water, and distilled water, or ultrapure water can be used for water. Moreover, by using the water which sterilized by UV irradiation or hydrogen-peroxide addition, since generating of mold or bacteria can be prevented when carrying out the mothball of the watercolor pigment dispersion liquid, it is suitable.

[0028] The water-color-ink constituent by ink constituent this invention is used for the recording method which used the ink constituent. With the recording method using an ink constituent, the recording method by the writing implement with for example, an ink jet recording method, a pen, etc. and various kinds of other printing methods are held. Therefore, the water-color-ink constituent by this invention can be preferably used for the application of writing implements, such as for example, an aquosity pen, the ink jet record approach, printing, a stamp, etc.

[0029] The water-color-ink constituent by this invention comes to contain the above mentioned watercolor pigment dispersion liquid at least.

[0030] To an ink constituent, the water-color-ink constituent by this invention contains surface treatment carbon black in 1 – 15% of the weight of the range, and contains it in 2 – 10% of the weight of the range more preferably. It is advantageous that an ink constituent contains surface treatment carbon black in such range at the point that the ink constituent of usable viscosity can be obtained by the ink jet recording method, securing sufficient printing concentration.

[0031] As for the water-color-ink constituent by this invention, it is desirable to use water as the main solvent. Pure water, such as ion exchange water, ultrafiltration water, Milli Q water, and distilled water, or ultrapure water can be used for water. Moreover, by using the water which sterilized by UV irradiation or hydrogen-peroxide addition, since generating of mold or bacteria can be prevented when carrying out the mothball of the water-color-ink constituent, it is suitable.

[0032] As for a water-color-ink constituent, in the desirable mode of this invention, it is desirable that it is what has permeability [as / whose penetration time of an ink constituent is less than 1 second] to come [the above mentioned watercolor pigment dispersion liquid] when the coverage of the ink constituent to a record medium is 1 mg/cm².

[0033] Here, specifically, permeability [as / whose penetration time in case coverage is 1 mg/cm² is less than 1 second] means the case where time amount even if it touches a printing side, until it stops becoming dirty with an ink constituent is less than 1 second, when the ink constituent of 50ng(s) is applied to the area of 360dpi(dots per inch) x360dpi at a regular paper. At this time, a neutral regular paper (a trade name, Fuji Xerox, Inc. make), for example, Xerox-P, is used as a regular paper.

[0034] The permeability of such an ink constituent can be acquired by improving the wettability to a record medium by adding an osmosis accelerator like the water-soluble organic solvent to

which the surface tension of a water solution is reduced, or a surfactant.

[0035] As such a water-soluble organic solvent, 1, such as carbitol [, such as cellosolves, such as lower alcohol such as ethanol and propanol, ethylene glycol monomethyl ether and ethylene glycol monoethyl ether, the diethylene-glycol monomethyl ether, and diethylene glycol monoethyl ether] and 1, 2-hexandiol, 1, and 2-octanediol, and 2-alkyl diols are mentioned, for example.

[0036] In the still more desirable mode of this invention, the water-soluble organic solvent of a glycol butyl ether system is more desirable as a water-soluble organic solvent used as an osmosis accelerator. As a water-soluble organic solvent of such a glycol butyl ether system, ethylene glycol mono-n-butyl ether, diethylene-glycol-n-butyl ether, triethylene glycol-n-butyl ether, etc. are mentioned, for example. By combining such a water-soluble organic solvent and surface treatment carbon black, the good printing object with which the blot at the time of printing was reduced can be offered.

[0037] As above surfactants, the Nonion nature surfactants, such as anionic surfactants, such as fatty-acid salts and alkyl-sulfuric-acid ester salts, polyoxyethylene alkyl ether, and polyoxyethylene phenyl ether, a cationic surfactant, both ionic surfactants, etc. are mentioned, for example.

[0038] As a more desirable surface active agent, the Nonion nature surface active agents, such as polyoxyethylene alkyl ether and polyoxyethylene phenyl ether, are mentioned. These are advantageous from the point that foaming of ink can be reduced as compared with the surfactant of ionicity. As an example of such a Nonion nature surfactant, Nissan Nonion K-211, K-220, P-213, E-215, E-220, S-215, S-220, HS-220, NS-212, NS-220 (all are a trade name and the Nippon Oil & Fats Co., Ltd. make above), etc. are mentioned. As an example of a still more desirable surfactant, acetylene glycol system surfactants, such as SAFI Norians 61 and 82,104,440,465,485 (all are trade name and air products - and made in - Chemicals above), are mentioned in the Nonion nature surfactant. Since foaming stops almost producing these when it adds to an ink constituent, it is suitable especially when using an ink constituent in the ink jet record approach.

[0039] in addition, the ink constituent according to this invention since distribution and/or the dissolution are possible for the surface treatment carbon black in this invention in water, without using a dispersant like a surfactant — setting — business — **** — these surfactants can be chosen only for the purpose of an osmosis facilitatory effect. That is, although it is usually necessary to choose in consideration of the combination to which a pigment and each ingredient stick each other in order to give dispersibility to a pigment, in this invention, a surfactant can be chosen only in consideration of an osmosis facilitatory effect, without taking such a combination into consideration.

[0040] In this invention, it is independent as an osmosis accelerator about a water-soluble organic solvent or a surfactant which was described above, or it is desirable by using together and using them to adjust preferably less than 40 mN/m of surface tension of an ink constituent to less than 35 mN/m.

[0041] The water-color-ink constituent by this invention becomes unable to include a moisturizer further for the purpose of ink desiccation prevention at the tip of the nozzle which carries out the regurgitation of the ink, when it uses for the ink jet record approach.

[0042] Such a moisturizer is usually chosen from a water-soluble and hygroscopic high ingredient. Specifically For example, a glycerol, ethylene glycol, a diethylene glycol, Triethylene glycol, a polyethylene glycol, propylene glycol, Dipropylene glycol, a polypropylene glycol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, Polyols, such as 1, 2, 6-hexane triol, and pentaerythritol Saccharides, such as ureas, such as lactams [, such as 2-pyrrolidone a N-methyl-2-pyrrolidone, and epsilon caprolactam], urea, thiourea, ethylene urea, 1, and 3-dimethyl imidazolidinone, maltitol, a sorbitol, glucono lactone, and a maltose, are mentioned.

[0043] These moisturizers can add the viscosity of an ink constituent to the ink constituent by this invention by using together with other ink additives in an amount which becomes 25 or less mPa-s at 25 degrees C.

[0044] In the water-color-ink constituent by this invention, a fixing agent, pH regulator, an antioxidant, an ultraviolet ray absorbent, antiseptics, an antifungal agent, etc. can be added

further if needed.

[0045] Water-soluble resin can be used as a fixing agent. As such a fixing agent, for example Water-soluble rosin and alginic acids Polyvinyl alcohol, hydroxypropylcellulose, a carboxymethyl cellulose, Hydroxyethyl cellulose, methyl cellulose, styrene-acrylic acid resin, Styrene-acrylic-acid-acrylic ester resin, styrene-maleic resin, Styrene-maleic-acid half ester resin, acrylic-acid-acrylic ester resin, Isobutylene-maleic resin, rosin denaturation maleic resin, a polyvinyl pyrrolidone, gum arabic starch, the poly allylamine, a polyvinyl amine, polyethyleneimine, etc. are mentioned. In addition, without using for the surface treatment carbon black of this invention the dispersant which consists of water soluble resin, since it is the coloring agent in which distribution and/or the dissolution are possible, the water soluble resin used in the ink of this invention can be chosen as water only for the purpose of the fixing effectiveness. That is, although it is necessary to choose in the combination to which a pigment and each ingredient stick each other in order to usually give dispersibility to a pigment, in this invention, it can choose only in consideration of fixable, without taking combination into consideration.

[0046] As a pH regulator, the hydroxide or amines of alkali metal, such as a lithium hydroxide, a sodium hydroxide, a potassium hydroxide, triethanolamine, and diethanolamine, are mentioned, for example.

[0047] as an anti-oxidant and an ultraviolet ray absorbent — aloha — NETO and methyl aloha — NETO etc. — aloha, the oxide of Ciba-Geigy Tinuvin(s) 328, 900, 1130, 384, 292, 123, 144, 622, 770, and 292, such as L-ascorbic acid, such as biurets, such as NETO, biuret, dimethyl biuret, and tetramethyl biuret, and a salt of those, Irgacor 252 and 153, Irganox 1010, 1076, and 1035, MD1024, or a lanthanide etc. is mentioned.

[0048] As antiseptics and an antifungal agent, sodium benzoate, pentachlorophenol sodium, 2-pyridine thiol-1-oxide sodium, sodium sorbate, sodium-dehydroacetate, 1, and 2-JIBENJISO thiazoline-3-ON (pro cheating-on-the-fare XL- the pro cheating on the fare CRL of ICI, the pro cheating on the fare BDN, the pro cheating on the fare GXL, 2, pro cheating on the fare TN) etc. is mentioned, for example.

[0049] The ink constituent by record approach this invention is used for the recording method which an ink constituent is made to adhere and prints to a record medium.

[0050] According to another mode of this invention, the ink jet record approach of printing by making the drop of the ink constituent by this invention adhering to a discharge record medium is offered. As the ink jet record approach by this invention, an ink constituent is breathed out as a drop from a detailed nozzle, and if it is the approach of making the drop adhering to a record medium, any approaches can be used. The approach of various modes is learned as an example of such an approach.

[0051] As an example of such an approach, an electrostatic suction method is held, for example. By this method, carry out the seal of approval of the strong electric field between the accelerating electrodes placed ahead of the nozzle and the nozzle, and ink is made to inject that it is liquid drop-like and continuously from a nozzle, and while an ink droplet flies between deflecting electrodes, a printing information signal is given and recorded on a deflecting electrode. Moreover, you may make it inject corresponding to a printing information signal, without deflecting an ink droplet if needed in this approach. There is a method of making an ink droplet inject compulsorily by applying a pressure to liquid ink with a small pump, and vibrating a nozzle mechanically with a quartz resonator etc. as other modes. By this approach, the injected ink droplet electrifies injection and coincidence, and while an ink droplet flies between deflecting electrodes, it gives and records a printing information signal on a deflecting electrode. The approach using a piezoelectric device as another mode is mentioned. By this approach, a pressure and a printing information signal are added to liquid ink by the piezoelectric device at coincidence, and it records by making an ink droplet inject. As still more nearly another mode, there is the approach of carrying out cubical expansion of the liquid ink rapidly according to an operation of heat energy. By this approach, according to a printing information signal, heating foaming of the liquid ink is carried out with microelectrode, and it records by making an ink droplet inject. According to the ink jet record approach by this invention, ink jet record can be performed stably.

[0052] Furthermore, according to this invention, the record object recorded by these record approaches is also offered.

[0053]

[Example] although the following examples explain this invention to a detail below, this invention is not ** limited to these.

[0054] The ratio of the adjustment pigment dispersion-liquid 1 specific surface area / DBP oil absorption of pigment dispersion liquid mixed color black FW18 (trade name, Degussa AG make) 35g of the carbon black of 1.63 in 1kg of water, and ground with the ball mill by zirconia beads. 500g of sodium hypochlorites was added to this grinding undiluted solution, it boiled for 10 hours, and wet oxidation was performed. The obtained distributed undiluted solution was filtered by glass fiber filter paper GA-100 (a trade name, ADVANTEC Oriental incorporated company make), and was washed further with water. The obtained wet cake was re-distributed in 5kg of water, it desalted and refined until electric conductivity became 2 mS/cm by the reverse osmotic membrane, it condensed until pigment concentration became 10% of the weight further, and pigment dispersion liquid 1 were adjusted.

[0055] The ratio of pigment dispersion-liquid 2 specific surface area / DBP oil absorption mixed color black S170 (trade name, Degussa AG make) 40g of the carbon black of 1.33 in 1kg of water, and ground with the ball mill by zirconia beads. Added 500g of sodium hypochlorites to this grinding undiluted solution, while the ball mill ground, it was made to react for 5 hours, and stirring further, it boiled for 4 hours and wet oxidation was performed. The obtained distributed undiluted solution was filtered by glass fiber filter paper GA-100 (a trade name, ADVANTEC Oriental incorporated company make), and was washed further with water. The obtained wet cake was re-distributed in 5kg of water, it desalted and refined until electric conductivity became 2 mS/cm by the reverse osmotic membrane, it condensed until pigment concentration became 10% of the weight further, and pigment dispersion liquid 2 were adjusted.

[0056] The ratio of pigment dispersion-liquid 3 specific surface area / DBP oil absorption mixed KONDAKU tex SC(trade name, Colombia carbon company make)40g of the carbon black of 1.91 in 1kg of water, and ground with the ball mill by zirconia beads. 500g of sodium hypochlorites was added to this grinding undiluted solution, it boiled for 10 hours, and wet oxidation was performed. The obtained distributed undiluted solution was filtered by glass fiber filter paper GA-100 (a trade name, ADVANTEC Oriental incorporated company make), and was washed further with water. The obtained wet cake was re-distributed in 5kg of water, it desalted and refined until electric conductivity became 2 mS/cm by the reverse osmotic membrane, it condensed until pigment concentration became 10% of the weight further, and pigment dispersion liquid 3 were adjusted.

[0057] The ratio of pigment dispersion-liquid 4 specific surface area / DBP oil absorption mixed #40 (trade name, Mitsubishi Chemical, Inc. make) 60g of the carbon black of 1.14 in 1kg of water, and ground with the ball mill by zirconia beads. Added 500g of sodium hypochlorites to this grinding undiluted solution, while the ball mill ground, it was made to react for 5 hours, and stirring further, it boiled for 4 hours and wet oxidation was performed. The obtained distributed undiluted solution was filtered by glass fiber filter paper GA-100 (a trade name, ADVANTEC Oriental incorporated company make), and was washed further with water. The obtained wet cake was re-distributed in 5kg of water, it desalted and refined until electric conductivity became 2 mS/cm by the reverse osmotic membrane, it condensed until pigment concentration became 10% of the weight further, and pigment dispersion liquid 4 were adjusted.

[0058] The ratio of pigment dispersion-liquid 5 specific surface area / DBP oil absorption mixed KONDAKU tex SC(trade name, Colombia carbon company make)40g of the carbon black of 1.91 in 1kg of water, and ground with the ball mill by zirconia beads. 500g of sodium hypochlorites was added to this grinding undiluted solution, it boiled for 10 hours, and wet oxidation was performed. The obtained distributed undiluted solution was filtered by glass fiber filter paper GA-100 (a trade name, ADVANTEC Oriental incorporated company make), and was washed further with water. The obtained wet cake was re-distributed in 5kg of water, it desalted and refined until electric conductivity became 2 mS/cm by the reverse osmotic membrane, it condensed until pigment concentration became 15% of the weight further, and pigment dispersion liquid 5 were

adjusted.

[0059] The ratio of pigment dispersion-liquid 6 specific surface area / DBP oil absorption mixed Rahaeng 1255 (trade name, Colombia carbon company make) 100g of the carbon black of 1.97 to N-methyl pyrrolidone 5kg, and ground with the ball mill by zirconia beads. 50g of sulfamic acid was added to this grinding undiluted solution, and it sulfonated at 150 degrees C for 10 hours. The whole quantity was supplied to 10kg of ice, the distributed undiluted solution was filtered by glass fiber filter paper GA-100 (a trade name, ADVANTEC Oriental incorporated company make), and it re-distributed in 5kg of water further, and it was filtered and washed. The obtained wet cake was re-distributed in 2kg of water, it desalted and refined until electric conductivity became 2 mS/cm by the reverse osmotic membrane, it condensed until pigment concentration became 15% of the weight further, and pigment dispersion liquid 6 were adjusted.

[0060] The ratio of pigment dispersion-liquid 7 specific surface area / DBP oil absorption mixed color black FW18 (trade name, Degussa AG make) 35g of the carbon black of 1.63 in 1kg of water, and ground with the ball mill by zirconia beads. 500g of sodium hypochlorites was added to this grinding undiluted solution, it boiled for 10 hours, and wet oxidation was performed. The obtained distributed undiluted solution was filtered by glass fiber filter paper GA-100 (a trade name, ADVANTEC Oriental incorporated company make), and was washed further with water. The obtained wet cake was re-distributed in 5kg of water, it desalted and refined until electric conductivity became 2 mS/cm by the reverse osmotic membrane, it condensed until pigment concentration became 15% of the weight further, and pigment dispersion liquid 7 were adjusted.

[0061] The ratio of pigment dispersion-liquid 8 specific surface area / DBP oil absorption mixed color black S170 (trade name, Degussa AG make) 40g of the carbon black of 1.33 in 1kg of water, and ground with the ball mill by zirconia beads. Added 500g of sodium hypochlorites to this grinding undiluted solution, while the ball mill ground, it was made to react for 5 hours, and stirring further, it boiled for 4 hours and wet oxidation was performed. The obtained distributed undiluted solution was filtered by glass fiber filter paper GA-100 (a trade name, ADVANTEC Oriental incorporated company make), and was washed further with water. The obtained wet cake was re-distributed in 5kg of water, it desalted and refined until electric conductivity became 2 mS/cm by the reverse osmotic membrane, it condensed until pigment concentration became 15% of the weight further, and pigment dispersion liquid 8 were adjusted.

[0062] The ratio of pigment dispersion-liquid 9 (example of comparison) specific surface area / DBP oil absorption mixed #45L(trade name, Mitsubishi Chemical, Inc. make)100g of the carbon black of 2.56 in 1kg of water, and ground with the ball mill by zirconia beads. Added 500g of sodium hypochlorites to this grinding undiluted solution, while the ball mill ground, it was made to react for 5 hours, and stirring further, it boiled for 4 hours and wet oxidation was performed. The obtained distributed undiluted solution was filtered by glass fiber filter paper GA-100 (a trade name, ADVANTEC Oriental incorporated company make), and was washed further with water. The obtained wet cake was re-distributed in 5kg of water, it desalted and refined until electric conductivity became 2 mS/cm by the reverse osmotic membrane, it condensed until pigment concentration became 10% of the weight further, and pigment dispersion liquid 9 were adjusted.

[0063] The ratio of pigment dispersion-liquid 10 (example of comparison) specific surface area / DBP oil absorption mixed Rahaeng 16 (trade name, Colombia carbon company make) 300g of the carbon black of 0.24 in 1kg of water, and ground with the ball mill by zirconia beads. Added 300g of sodium hypochlorites to this grinding undiluted solution, while the ball mill ground, it was made to react for 5 hours, and stirring further, it boiled for 4 hours and wet oxidation was performed. The obtained distributed undiluted solution was filtered by glass fiber filter paper GA-100 (a trade name, ADVANTEC Oriental incorporated company make), and was washed further with water. The obtained wet cake was re-distributed in 5kg of water, it desalted and refined until electric conductivity became 2 mS/cm by the reverse osmotic membrane, it condensed until pigment concentration became 10% of the weight further, and pigment dispersion liquid 10 were adjusted.

[0064] Color black FW18 (trade name, Degussa AG make) 100g used in the pigment dispersion-liquid 11 (example of a comparison) example 1, JON krill J-62 (trade name, Johnson polymer company make) 150g of the dispersant of water soluble resin, 6g of sodium hydroxides, and 250g

of water were mixed, and the ball mill by zirconia beads performed distribution for 10 hours. The obtained distributed undiluted solution was filtered with the filter made from stainless steel of about 5 micrometers of apertures, it diluted until pigment concentration became 10% of the weight with water, and the pigment dispersion liquid 11 distributed with water soluble resin were adjusted.

[0065] Ethanol 4g was mixed as glycerol 5g, 2-pyrrolidone 5g, and an osmosis promotion component as 20g (pigment dispersion liquid 1) of watercolor pigment dispersion liquid which the ink constituent created adjustment ink constituent 1, and a moisturizing component, and the whole quantity added ultrapure water to 100g. This mixed liquor was stirred for 2 hours, it filtered with the filter made from stainless steel of about 5 micrometers of apertures, and the ink constituent 1 was prepared.

[0066] Ethanol 4g was mixed as triethylene glycol 6g, 5g of ureas, and an osmosis promotion component as 20g (pigment dispersion liquid 2) of watercolor pigment dispersion liquid created ink constituent 2, and a moisturizing component, and the whole quantity added ultrapure water to 100g. This mixed liquor was stirred for 2 hours, it filtered with the filter made from stainless steel of about 5 micrometers of apertures, and the ink constituent 2 was prepared.

[0067] Ink constituent 3 pigment dispersion liquid 5 were mixed as 45g and a moisturizing component, tert-pentanol 4g and Nissan Nonion NS-220(trade name, Nippon Oil & Fats Co., Ltd. make) 1g of the Nonion nature surfactant were mixed as glycerol 10g, 2-pyrrolidone 5g, and an osmosis promotion component, ultrapure water was added, the whole quantity was set to 100g, and triethanolamine was added until Ink pH was further set to 7.5. This mixed liquor was stirred for 2 hours, it filtered with the filter made from stainless steel of about 5 micrometers of apertures, and the ink constituent 3 was prepared.

[0068] Ink constituent 4 pigment dispersion liquid 6 were mixed as 45g and a moisturizer, Nissan Nonion NS-210 (trade name, Nippon Oil & Fats Co., Ltd. make) 2.5g of the Nonion nature surfactant was mixed as triethylene glycol 10g, diethylene-glycol 5g, and an osmosis accelerator, ultrapure water was added, the whole quantity was set to 100g, and triethanolamine was added until Ink pH was further set to 7.5. This mixed liquor was stirred for 2 hours, it filtered with the filter made from stainless steel of about 5 micrometers of apertures, and the ink constituent 4 was prepared.

[0069] Ink constituent 5 pigment dispersion liquid 7 were mixed as 45g and a moisturizing component, tert-pentanol 4g and Nissan Nonion NS-220(trade name, Nippon Oil & Fats Co., Ltd. make) 1g of the Nonion nature surfactant were mixed as glycerol 10g, 2-pyrrolidone 5g, and an osmosis promotion component, ultrapure water was added, the whole quantity was set to 100g, and triethanolamine was added until Ink pH was further set to 7.5. This mixed liquor was stirred for 2 hours, it filtered with the filter made from stainless steel of about 5 micrometers of apertures, and the ink constituent 5 was prepared.

[0070] Ink constituent 6 pigment dispersion liquid 8 were mixed as 45g and a moisturizer, Nissan Nonion NS-210 (trade name, Nippon Oil & Fats Co., Ltd. make) 2.5g of the Nonion nature surfactant was mixed as triethylene glycol 10g, diethylene-glycol 5g, and an osmosis accelerator, ultrapure water was added, the whole quantity was set to 100g, and triethanolamine was added until Ink pH was further set to 7.5. This mixed liquor was stirred for 2 hours, it filtered with the filter made from stainless steel of about 5 micrometers of apertures, and the ink constituent 6 was prepared.

[0071] Ink constituent 7 pigment dispersion liquid 8 were mixed as 45g and a moisturizer, diethylene-glycol-Monod n-butyl ether 7.5g was mixed as glycerol 10g, diethylene-glycol 5g, and an osmosis accelerator, ultrapure water was added, the whole quantity was set to 100g, and triethanolamine was added until Ink pH was further set to 7.3. This mixed liquor was stirred for 2 hours, it filtered with the filter made from stainless steel of about 5 micrometers of apertures, and the ink constituent 7 was prepared.

[0072] Ink constituent 8 pigment dispersion liquid 7 were mixed as 45g and a moisturizer, triethylene glycol-Monod n-butyl ether 5g was mixed as glycerol 10g, 1,5-pentanediol 5g, and an osmosis accelerator, ultrapure water was added, the whole quantity was set to 100g, and triethanolamine was added until Ink pH was further set to 7.3. This mixed liquor was stirred for 2

hours, it filtered with the filter made from stainless steel of about 5 micrometers of apertures, and the ink constituent 8 was prepared.

[0073] 0.3g and SAFI Norian 485 were mixed for SAFI Norian 104 of an acetylene glycol system surfactant as 45g and a moisturizer, 1.5g was mixed for ink constituent 9 pigment dispersion liquid 7 as glycerol 7.5g, 1,5-pentanediol 7.5g, and an osmosis accelerator, ultrapure water was added, the whole quantity was set to 100g, and triethanolamine was added until Ink pH was further set to 7.3. This mixed liquor was stirred for 2 hours, it filtered with the filter made from stainless steel of about 5 micrometers of apertures, and the ink constituent 9 was prepared.

[0074] SAFI Norian 465 of diethylene-glycol-Monod n-butyl ether 5g and an acetylene glycol system surfactant was mixed as 45g and a moisturizer, 1g was mixed for ink constituent 10 pigment dispersion liquid 8 as glycerol 10g, diethylene-glycol 5g, and an osmosis accelerator, ultrapure water was added, the whole quantity was set to 100g, and triethanolamine was added until Ink pH was further set to 7.2. This mixed liquor was stirred for 2 hours, it filtered with the filter made from stainless steel of about 5 micrometers of apertures, and the ink constituent 10 was prepared.

[0075] The ink constituent 11 was prepared by the same approach as the case of the ink constituent 1 except using ink constituent 11 (example of comparison) pigment dispersion liquid 9.

[0076] The ink constituent 12 was prepared by the same approach as the case of the ink constituent 1 except using ink constituent 12 (example of comparison) pigment dispersion liquid 10.

[0077] The ink constituent 13 was prepared by the same approach as the case of the ink constituent 1 except using ink constituent 13 (example of comparison) pigment dispersion liquid 11.

[0078] The ratio of ink constituent 14 (example of comparison) specific surface area / DBP oil absorption mixed #45L(trade name, Mitsubishi Chemical, Inc. make)300g of the carbon black of 2.56 in 1kg of water, and ground with the ball mill by zirconia beads. Added 450g of sodium hypochlorites to this grinding undiluted solution, while the ball mill ground, it was made to react for 5 hours, and stirring further, it boiled for 4 hours and wet oxidation was performed. The obtained distributed undiluted solution was filtered by glass fiber filter paper GA-100 (a trade name, ADVANTEC Oriental incorporated company make), and was washed further with water. The obtained wet cake was re-distributed in 5kg of water, it desalted and refined until electric conductivity became 2 mS/cm by the reverse osmotic membrane, it condensed until pigment concentration became 15% of the weight further, and pigment dispersion liquid were adjusted. The ink constituent 14 was created like the case of the ink constituent 7 using 45g of these pigment dispersion liquid.

[0079] The ratio of ink constituent 15 (example of comparison) specific surface area / DBP oil absorption mixed Rahaeng 16 (trade name, Colombia carbon company make) 300g of the carbon black of 0.24 in 1kg of water, and ground with the ball mill by zirconia beads. Added 300g of sodium hypochlorites to this grinding undiluted solution, while the ball mill ground, it was made to react for 5 hours, and stirring further, it boiled for 4 hours and wet oxidation was performed. The obtained distributed undiluted solution was filtered by glass fiber filter paper GA-100 (a trade name, ADVANTEC Oriental incorporated company make), and was washed further with water. The obtained wet cake was re-distributed in 5kg of water, it desalted and refined until electric conductivity became 2 mS/cm by the reverse osmotic membrane, it condensed until pigment concentration became 15% of the weight further, and pigment dispersion liquid were adjusted. The ink constituent 15 was created like the case of the ink constituent 7 using 45g of these pigment dispersion liquid.

[0080] Apply each of the evaluation pigment dispersion liquid 1-4 of pigment dispersion liquid, and pigment dispersion liquid 9-11 to Xerox-P (a trade name, Fuji Xerox, Inc. make) of a neutral regular paper with an applicator with a spreading thickness of 25 micrometers, it was made to dry, and each OD value was measured using Macbeth concentration meter TR-927 (a trade name, COL mho gene company make). The result was as being shown in Table 1.

[0081]

Table 1 Pigment dispersion liquid The ratio of specific surface area / DBP oil absorption OD value 1 1.63 1.53 2 1.33 1.55 3 1.91 1.45 4 1.14 1.47 9 2.56 1.30 10 0.24 1.25 11 1.63 1.32 About each of the evaluation 1 ink constituents 1 and 2 of an ink constituent, and the ink constituents 11-13 piezoelectric-device type on-demand mold ink jet recording device MJ-500 (a trade name --) It printed by the Seiko Epson, Inc. make to Xerox-P (a trade name, Fuji Xerox, Inc. make) of a neutral regular paper, and each OD value was measured after desiccation by Macbeth concentration meter TR-927 (a trade name, COL mho gene company make). The result was as being shown in Table 2.

[0082]

Table 2 Ink constituent Ratio of specific surface area / DBP oil absorption OD value 1 1.53 1.55 2 1.33 1.55 11 2.56 1.31 12 0.24 1.33 13 1.63 1.38 About each of the ink constituents 3-10 which have the permeability whose penetration time of evaluation 2 ink of an ink constituent is less than 1 second, and the ink constituents 14 and 15 piezoelectric-device type on-demand mold ink jet recording device MJ-930C (a trade name --) By the Seiko Epson, Inc. make, it printed to Xerox-P (a trade name, Fuji Xerox, Inc. make) of a neutral regular paper, and each OD value was measured after desiccation using Macbeth concentration meter TR-927 (a trade name, COL mho gene company make). The result was as being shown in Table 3.

[0083]

Table 3 Ink constituent Ratio of specific surface area / DBP oil absorption OD value 3 1.91 1.40 4 1.97 1.37 5 1.63 1.42 6 1.33 1.44 7 1.33 1.44 8 1.63 1.42 9 1.63 1.43 10 1.33 1.47 14 2.56 1.17 15 0.24 1.24 About each printing object obtained by the evaluation 3 aforementioned evaluation 2 of an ink constituent, the quality of printed character (for example, blot of a printing object) was evaluated by viewing.

[0084] The printing object of the ink constituents 7 and 8 which added glycol butyl ether as an osmosis accelerator had few blots of the circumference part of printing, and especially the quality of printed character was good.

[Translation done.]

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- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

EXAMPLE

[Example] although the following examples explain this invention to a detail below, this invention is not ** limited to these.

[0054] The ratio of the adjustment pigment dispersion-liquid 1 specific surface area / DBP oil absorption of pigment dispersion liquid mixed color black FW18 (trade name, Degussa AG make) 35g of the carbon black of 1.63 in 1kg of water, and ground with the ball mill by zirconia beads. 500g of sodium hypochlorites was added to this grinding undiluted solution, it boiled for 10 hours, and wet oxidation was performed. The obtained distributed undiluted solution was filtered by glass fiber filter paper GA-100 (a trade name, ADVANTEC Oriental incorporated company make), and was washed further with water. The obtained wet cake was re-distributed in 5kg of water, it desalted and refined until electric conductivity became 2 mS/cm by the reverse osmotic membrane, it condensed until pigment concentration became 10% of the weight further, and pigment dispersion liquid 1 were adjusted.

[0055] The ratio of pigment dispersion-liquid 2 specific surface area / DBP oil absorption mixed color black S170 (trade name, Degussa AG make) 40g of the carbon black of 1.33 in 1kg of water, and ground with the ball mill by zirconia beads. Added 500g of sodium hypochlorites to this grinding undiluted solution, while the ball mill ground, it was made to react for 5 hours, and stirring further, it boiled for 4 hours and wet oxidation was performed. The obtained distributed undiluted solution was filtered by glass fiber filter paper GA-100 (a trade name, ADVANTEC Oriental incorporated company make), and was washed further with water. The obtained wet cake was re-distributed in 5kg of water, it desalted and refined until electric conductivity became 2 mS/cm by the reverse osmotic membrane, it condensed until pigment concentration became 10% of the weight further, and pigment dispersion liquid 2 were adjusted.

[0056] The ratio of pigment dispersion-liquid 3 specific surface area / DBP oil absorption mixed KONDAKU tex SC(trade name, Colombia carbon company make)40g of the carbon black of 1.91 in 1kg of water, and ground with the ball mill by zirconia beads. 500g of sodium hypochlorites was added to this grinding undiluted solution, it boiled for 10 hours, and wet oxidation was performed. The obtained distributed undiluted solution was filtered by glass fiber filter paper GA-100 (a trade name, ADVANTEC Oriental incorporated company make), and was washed further with water. The obtained wet cake was re-distributed in 5kg of water, it desalted and refined until electric conductivity became 2 mS/cm by the reverse osmotic membrane, it condensed until pigment concentration became 10% of the weight further, and pigment dispersion liquid 3 were adjusted.

[0057] The ratio of pigment dispersion-liquid 4 specific surface area / DBP oil absorption mixed #40 (trade name, Mitsubishi Chemical, Inc. make) 60g of the carbon black of 1.14 in 1kg of water, and ground with the ball mill by zirconia beads. Added 500g of sodium hypochlorites to this grinding undiluted solution, while the ball mill ground, it was made to react for 5 hours, and stirring further, it boiled for 4 hours and wet oxidation was performed. The obtained distributed undiluted solution was filtered by glass fiber filter paper GA-100 (a trade name, ADVANTEC Oriental incorporated company make), and was washed further with water. The obtained wet cake was re-distributed in 5kg of water, it desalted and refined until electric conductivity became 2 mS/cm by the reverse osmotic membrane, it condensed until pigment concentration

became 10% of the weight further, and pigment dispersion liquid 4 were adjusted.

[0058] The ratio of pigment dispersion-liquid 5 specific surface area / DBP oil absorption mixed KONDAKU tex SC(trade name, Colombia carbon company make)40g of the carbon black of 1.91 in 1kg of water, and ground with the ball mill by zirconia beads. 500g of sodium hypochlorites was added to this grinding undiluted solution, it boiled for 10 hours, and wet oxidation was performed. The obtained distributed undiluted solution was filtered by glass fiber filter paper GA-100 (a trade name, ADVANTEC Oriental incorporated company make), and was washed further with water. The obtained wet cake was re-distributed in 5kg of water, it desalted and refined until electric conductivity became 2 mS/cm by the reverse osmotic membrane, it condensed until pigment concentration became 15% of the weight further, and pigment dispersion liquid 5 were adjusted.

[0059] The ratio of pigment dispersion-liquid 6 specific surface area / DBP oil absorption mixed Rahaeng 1255 (trade name, Colombia carbon company make) 100g of the carbon black of 1.97 to N-methyl pyrrolidone 5kg, and ground with the ball mill by zirconia beads. 50g of sulfamic acid was added to this grinding undiluted solution, and it sulfonated at 150 degrees C for 10 hours. The whole quantity was supplied to 10kg of ice, the distributed undiluted solution was filtered by glass fiber filter paper GA-100 (a trade name, ADVANTEC Oriental incorporated company make), and it re-distributed in 5kg of water further, and it was filtered and washed. The obtained wet cake was re-distributed in 2kg of water, it desalted and refined until electric conductivity became 2 mS/cm by the reverse osmotic membrane, it condensed until pigment concentration became 15% of the weight further, and pigment dispersion liquid 6 were adjusted.

[0060] The ratio of pigment dispersion-liquid 7 specific surface area / DBP oil absorption mixed color black FW18 (trade name, Degussa AG make) 35g of the carbon black of 1.63 in 1kg of water, and ground with the ball mill by zirconia beads. 500g of sodium hypochlorites was added to this grinding undiluted solution, it boiled for 10 hours, and wet oxidation was performed. The obtained distributed undiluted solution was filtered by glass fiber filter paper GA-100 (a trade name, ADVANTEC Oriental incorporated company make), and was washed further with water. The obtained wet cake was re-distributed in 5kg of water, it desalted and refined until electric conductivity became 2 mS/cm by the reverse osmotic membrane, it condensed until pigment concentration became 15% of the weight further, and pigment dispersion liquid 7 were adjusted.

[0061] The ratio of pigment dispersion-liquid 8 specific surface area / DBP oil absorption mixed color black S170 (trade name, Degussa AG make) 40g of the carbon black of 1.33 in 1kg of water, and ground with the ball mill by zirconia beads. Added 500g of sodium hypochlorites to this grinding undiluted solution, while the ball mill ground, it was made to react for 5 hours, and stirring further, it boiled for 4 hours and wet oxidation was performed. The obtained distributed undiluted solution was filtered by glass fiber filter paper GA-100 (a trade name, ADVANTEC Oriental incorporated company make), and was washed further with water. The obtained wet cake was re-distributed in 5kg of water, it desalted and refined until electric conductivity became 2 mS/cm by the reverse osmotic membrane, it condensed until pigment concentration became 15% of the weight further, and pigment dispersion liquid 8 were adjusted.

[0062] The ratio of pigment dispersion-liquid 9 (example of comparison) specific surface area / DBP oil absorption mixed #45L(trade name, Mitsubishi Chemical, Inc. make)100g of the carbon black of 2.56 in 1kg of water, and ground with the ball mill by zirconia beads. Added 500g of sodium hypochlorites to this grinding undiluted solution, while the ball mill ground, it was made to react for 5 hours, and stirring further, it boiled for 4 hours and wet oxidation was performed. The obtained distributed undiluted solution was filtered by glass fiber filter paper GA-100 (a trade name, ADVANTEC Oriental incorporated company make), and was washed further with water. The obtained wet cake was re-distributed in 5kg of water, it desalted and refined until electric conductivity became 2 mS/cm by the reverse osmotic membrane, it condensed until pigment concentration became 10% of the weight further, and pigment dispersion liquid 9 were adjusted.

[0063] The ratio of pigment dispersion-liquid 10 (example of comparison) specific surface area / DBP oil absorption mixed Rahaeng 16 (trade name, Colombia carbon company make) 300g of the carbon black of 0.24 in 1kg of water, and ground with the ball mill by zirconia beads. Added 300g of sodium hypochlorites to this grinding undiluted solution, while the ball mill ground, it was made

to react for 5 hours, and stirring further, it boiled for 4 hours and wet oxidation was performed. The obtained distributed undiluted solution was filtered by glass fiber filter paper GA-100 (a trade name, ADVANTEC Oriental incorporated company make), and was washed further with water. The obtained wet cake was re-distributed in 5kg of water, it desalted and refined until electric conductivity became 2 mS/cm by the reverse osmotic membrane, it condensed until pigment concentration became 10% of the weight further, and pigment dispersion liquid 10 were adjusted.

[0064] Color black FW18 (trade name, Degussa AG make) 100g used in the pigment dispersion-liquid 11 (example of a comparison) example 1, JON krill J-62 (trade name, Johnson polymer company make) 150g of the dispersant of water soluble resin, 6g of sodium hydroxides, and 250g of water were mixed, and the ball mill by zirconia beads performed distribution for 10 hours. The obtained distributed undiluted solution was filtered with the filter made from stainless steel of about 5 micrometers of apertures, it diluted until pigment concentration became 10% of the weight with water, and the pigment dispersion liquid 11 distributed with water soluble resin were adjusted.

[0065] Ethanol 4g was mixed as glycerol 5g, 2-pyrrolidone 5g, and an osmosis promotion component as 20g (pigment dispersion liquid 1) of watercolor pigment dispersion liquid which the ink constituent created adjustment ink constituent 1, and a moisturizing component, and the whole quantity added ultrapure water to 100g. This mixed liquor was stirred for 2 hours, it filtered with the filter made from stainless steel of about 5 micrometers of apertures, and the ink constituent 1 was prepared.

[0066] Ethanol 4g was mixed as triethylene glycol 6g, 5g of ureas, and an osmosis promotion component as 20g (pigment dispersion liquid 2) of watercolor pigment dispersion liquid created ink constituent 2, and a moisturizing component, and the whole quantity added ultrapure water to 100g. This mixed liquor was stirred for 2 hours, it filtered with the filter made from stainless steel of about 5 micrometers of apertures, and the ink constituent 2 was prepared.

[0067] Ink constituent 3 pigment dispersion liquid 5 were mixed as 45g and a moisturizing component, tert-pentanol 4g and Nissan Nonion NS-220(trade name, Nippon Oil & Fats Co., Ltd. make) 1g of the Nonion nature surfactant were mixed as glycerol 10g, 2-pyrrolidone 5g, and an osmosis promotion component, ultrapure water was added, the whole quantity was set to 100g, and triethanolamine was added until Ink pH was further set to 7.5. This mixed liquor was stirred for 2 hours, it filtered with the filter made from stainless steel of about 5 micrometers of apertures, and the ink constituent 3 was prepared.

[0068] Ink constituent 4 pigment dispersion liquid 6 were mixed as 45g and a moisturizer, Nissan Nonion NS-210 (trade name, Nippon Oil & Fats Co., Ltd. make) 2.5g of the Nonion nature surfactant was mixed as triethylene glycol 10g, diethylene-glycol 5g, and an osmosis accelerator, ultrapure water was added, the whole quantity was set to 100g, and triethanolamine was added until Ink pH was further set to 7.5. This mixed liquor was stirred for 2 hours, it filtered with the filter made from stainless steel of about 5 micrometers of apertures, and the ink constituent 4 was prepared.

[0069] Ink constituent 5 pigment dispersion liquid 7 were mixed as 45g and a moisturizing component, tert-pentanol 4g and Nissan Nonion NS-220(trade name, Nippon Oil & Fats Co., Ltd. make) 1g of the Nonion nature surfactant were mixed as glycerol 10g, 2-pyrrolidone 5g, and an osmosis promotion component, ultrapure water was added, the whole quantity was set to 100g, and triethanolamine was added until Ink pH was further set to 7.5. This mixed liquor was stirred for 2 hours, it filtered with the filter made from stainless steel of about 5 micrometers of apertures, and the ink constituent 5 was prepared.

[0070] Ink constituent 6 pigment dispersion liquid 8 were mixed as 45g and a moisturizer, Nissan Nonion NS-210 (trade name, Nippon Oil & Fats Co., Ltd. make) 2.5g of the Nonion nature surfactant was mixed as triethylene glycol 10g, diethylene-glycol 5g, and an osmosis accelerator, ultrapure water was added, the whole quantity was set to 100g, and triethanolamine was added until Ink pH was further set to 7.5. This mixed liquor was stirred for 2 hours, it filtered with the filter made from stainless steel of about 5 micrometers of apertures, and the ink constituent 6 was prepared.

[0071] Ink constituent 7 pigment dispersion liquid 8 were mixed as 45g and a moisturizer, diethylene-glycol-Monod n-butyl ether 7.5g was mixed as glycerol 10g, diethylene-glycol 5g, and an osmosis accelerator, ultrapure water was added, the whole quantity was set to 100g, and triethanolamine was added until Ink pH was further set to 7.3. This mixed liquor was stirred for 2 hours, it filtered with the filter made from stainless steel of about 5 micrometers of apertures, and the ink constituent 7 was prepared.

[0072] Ink constituent 8 pigment dispersion liquid 7 were mixed as 45g and a moisturizer, triethylene glycol-Monod n-butyl ether 5g was mixed as glycerol 10g, 1,5-pentanediol 5g, and an osmosis accelerator, ultrapure water was added, the whole quantity was set to 100g, and triethanolamine was added until Ink pH was further set to 7.3. This mixed liquor was stirred for 2 hours, it filtered with the filter made from stainless steel of about 5 micrometers of apertures, and the ink constituent 8 was prepared.

[0073] 0.3g and SAFI Norian 485 were mixed for SAFI Norian 104 of an acetylene glycol system surfactant as 45g and a moisturizer, 1.5g was mixed for ink constituent 9 pigment dispersion liquid 7 as glycerol 7.5g, 1,5-pentanediol 7.5g, and an osmosis accelerator, ultrapure water was added, the whole quantity was set to 100g, and triethanolamine was added until Ink pH was further set to 7.3. This mixed liquor was stirred for 2 hours, it filtered with the filter made from stainless steel of about 5 micrometers of apertures, and the ink constituent 9 was prepared.

[0074] SAFI Norian 465 of diethylene-glycol-Monod n-butyl ether 5g and an acetylene glycol system surfactant was mixed as 45g and a moisturizer, 1g was mixed for ink constituent 10 pigment dispersion liquid 8 as glycerol 10g, diethylene-glycol 5g, and an osmosis accelerator, ultrapure water was added, the whole quantity was set to 100g, and triethanolamine was added until Ink pH was further set to 7.2. This mixed liquor was stirred for 2 hours, it filtered with the filter made from stainless steel of about 5 micrometers of apertures, and the ink constituent 10 was prepared.

[0075] The ink constituent 11 was prepared by the same approach as the case of the ink constituent 1 except using ink constituent 11 (example of comparison) pigment dispersion liquid 9.

[0076] The ink constituent 12 was prepared by the same approach as the case of the ink constituent 1 except using ink constituent 12 (example of comparison) pigment dispersion liquid 10.

[0077] The ink constituent 13 was prepared by the same approach as the case of the ink constituent 1 except using ink constituent 13 (example of comparison) pigment dispersion liquid 11.

[0078] The ratio of ink constituent 14 (example of comparison) specific surface area / DBP oil absorption mixed #45L(trade name, Mitsubishi Chemical, Inc. make)300g of the carbon black of 2.56 in 1kg of water, and ground with the ball mill by zirconia beads. Added 450g of sodium hypochlorites to this grinding undiluted solution, while the ball mill ground, it was made to react for 5 hours, and stirring further, it boiled for 4 hours and wet oxidation was performed. The obtained distributed undiluted solution was filtered by glass fiber filter paper GA-100 (a trade name, ADVANTEC Oriental incorporated company make), and was washed further with water. The obtained wet cake was re-distributed in 5kg of water, it desalted and refined until electric conductivity became 2 mS/cm by the reverse osmotic membrane, it condensed until pigment concentration became 15% of the weight further, and pigment dispersion liquid were adjusted. The ink constituent 14 was created like the case of the ink constituent 7 using 45g of these pigment dispersion liquid.

[0079] The ratio of ink constituent 15 (example of comparison) specific surface area / DBP oil absorption mixed Rahaeng 16 (trade name, Colombia carbon company make) 300g of the carbon black of 0.24 in 1kg of water, and ground with the ball mill by zirconia beads. Added 300g of sodium hypochlorites to this grinding undiluted solution, while the ball mill ground, it was made to react for 5 hours, and stirring further, it boiled for 4 hours and wet oxidation was performed. The obtained distributed undiluted solution was filtered by glass fiber filter paper GA-100 (a trade name, ADVANTEC Oriental incorporated company make), and was washed further with water. The obtained wet cake was re-distributed in 5kg of water, it desalted and refined until electric

conductivity became 2 mS/cm by the reverse osmotic membrane, it condensed until pigment concentration became 15% of the weight further, and pigment dispersion liquid were adjusted. The ink constituent 15 was created like the case of the ink constituent 7 using 45g of these pigment dispersion liquid.

[0080] Apply each of the evaluation pigment dispersion liquid 1-4 of pigment dispersion liquid, and pigment dispersion liquid 9-11 to Xerox-P (a trade name, Fuji Xerox, Inc. make) of a neutral regular paper with an applicator with a spreading thickness of 25 micrometers, it was made to dry, and each OD value was measured using Macbeth concentration meter TR-927 (a trade name, COL mho gene company make). The result was as being shown in Table 1.

[0081]

Table 1 Pigment dispersion liquid The ratio of specific surface area / DBP oil absorption OD value 1 1.63 1.53 2 1.33 1.55 3 1.91 1.45 4 1.14 1.47 9 2.56 1.30 10 0.24 1.25 11 1.63 1.32 About each of the evaluation 1 ink constituents 1 and 2 of an ink constituent, and the ink constituents 11-13, it is by piezoelectric-device type on-demand mold ink jet recording device MJ-500 (a trade name, Seiko Epson, Inc. make). It printed to Xerox-P (a trade name, Fuji Xerox, Inc. make) of a neutral regular paper, and each OD value was measured after desiccation by Macbeth concentration meter TR-927 (a trade name, COL mho gene company make). The result was as being shown in Table 2.

[0082]

Table 2 Ink constituent Ratio of specific surface area / DBP oil absorption OD value 1 1.53 1.55 2 1.33 1.55 11 2.56 1.31 12 0.24 1.33 13 1.63 1.38 About each of the ink constituents 3-10 which have the permeability whose penetration time of evaluation 2 ink of an ink constituent is less than 1 second, and the ink constituents 14 and 15 Piezoelectric-device type on-demand mold ink jet recording device MJ-930C (a trade name, Seiko Epson, Inc. make) It printed to Xerox-P (a trade name, Fuji Xerox, Inc. make) of a neutral regular paper, and each OD value was measured after desiccation using Macbeth concentration meter TR-927 (a trade name, COL mho gene company make). The result was as being shown in Table 3.

[0083]

Table 3 Ink constituent Ratio of specific surface area / DBP oil absorption OD value 3 1.91 1.40 4 1.97 1.37 5 1.63 1.42 6 1.33 1.44 7 1.33 1.44 8 1.63 1.42 9 1.63 About each printing object obtained by the evaluation 3 aforementioned evaluation 2 of a 1.43 10 ink constituent, it is the quality of printed character (to for example, that of a printing object). 1.33 1.47 14 2.56 1.17 15 0.24 1.24 Viewing estimated ****.

[0084] The printing object of the ink constituents 7 and 8 which added glycol butyl ether as an osmosis accelerator had few blots of the circumference part of printing, and especially the quality of printed character was good.

[Translation done.]

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is drawing showing the outline of the vacuum pyrolysis equipment for measuring the amount of hydrophilic functional groups in surface treatment carbon black.

[Description of Notations]

- 1 Electric Furnace
- 2 Quartz Sample Tubing
- 3 Manometer
- 4 Freezing Trap
- 5 Vacuum Pump
- 6 Toepler Pump
- 7 Gas Buret
- 8 Gas Chromatograph
- 9 Carrier Gas Entrance
- 10 Recorder

[Translation done.]

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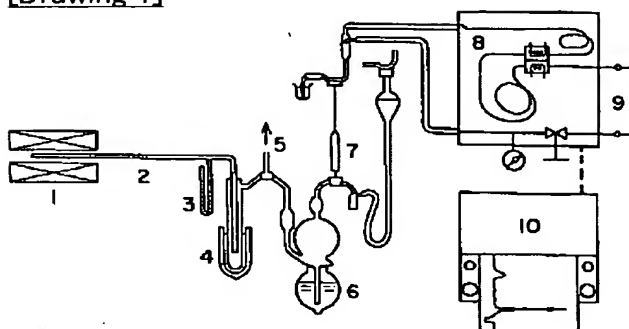
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DRAWINGS

[Drawing 1]



[Translation done.]

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(33) 優先権主張国 日本 (J P)

(71) 出願人 000002369

セイコーエプソン株式会社

東京都新宿区西新宿2丁目4番1号

(71) 出願人 000103895

オリエント化学工業株式会社

大阪府大阪市旭区新森1丁目7番14号

(72) 発明者 伊 藤 弘

長野県諏訪市大和三丁目3番5号 セイコーエプソン株式会社内

(74) 代理人 100064285

弁理士 佐藤 一雄 (外3名)

最終頁に続く

(54) 【発明の名称】 水性顔料分散液、水性インク組成物および前記インク組成物を用いた記録方法

(57) 【要約】

【課題】 印字濃度が高い水性顔料分散液ならびにインク組成物を提供することにある。

【解決手段】 水と、表面改質カーボンブラックとを少なくとも含んでなる水性顔料分散液であって、該表面改質カーボンブラックが、比表面積 (m^2/g) / DBP 吸油量 ($\text{ml}/100\text{g}$) の比が0.3~2.5であって、かつ、親水性官能基がその表面に導入され、その結果、分散剤無しに水に分散および/または溶解が可能とされたものである、水性顔料分散液。

(2)

【特許請求の範囲】

【請求項1】水と、表面改質カーボンブラックとを少なくとも含んでなる水性顔料分散液であって、該表面改質カーボンブラックが、比表面積 (m^2/g) / DBP吸油量 ($\text{ml}/100\text{g}$) の比が0.3～2.5であって、かつ、親水性官能基がその表面に導入され、その結果、分散剤無しに水に分散および/または溶解が可能とされたものである、水性顔料分散液。

【請求項2】前記表面改質カーボンブラックの、比表面積 (m^2/g) / DBP吸油量 ($\text{ml}/100\text{g}$) の比が0.3～1.75である、請求項1に記載の水性顔料分散液。

【請求項3】前記表面改質カーボンブラックが1.5 mmol/g 以上の親水性官能基を有するものである、請求項1または2に記載の水性顔料分散液。

【請求項4】請求項1～3のいずれか一項に記載の水性顔料分散液の製造方法であって、比表面積/DBP吸油量の比が0.3～2.5であるカーボンブラックを、次亜ハロゲン酸またはその塩を用いて湿式酸化して親水性官能基を導入し、分散剤無しに前記カーボンブラックを水に分散および/または溶解させる工程を含んでなる、方法。

【請求項5】請求項1～3のいずれか一項に記載の水性顔料分散液を少なくとも含んでなる、水性インク組成物。

【請求項6】記録媒体へのインク組成物の塗布量が1 mg/cm^2 であるとき、インク組成物の浸透時間が1秒未満であるような浸透性を有する、請求項5に記載のインク組成物。

【請求項7】インク組成物の表面張力が40 mN/m 未満である、請求項5または6に記載の水性インク組成物。

【請求項8】グリコールブチルエーテル系の水溶性有機溶剤をさらに含んでなる、請求項5～7のいずれか一項に記載の水性インク組成物。

【請求項9】ノニオン性界面活性剤をさらに含んでなる、請求項5～8のいずれか一項に記載の水性インク組成物。

【請求項10】ノニオン性界面活性剤がアセチレングリコール系界面活性剤である、請求項9に記載の水性インク組成物。

【請求項11】インク組成物を付着させて記録媒体に印字を行う記録方法であって、インク組成物として請求項5～10のいずれか一項に記載の水性インク組成物を用いる、記録方法。

【請求項12】インク組成物の液滴を吐出し、該液滴を記録媒体に付着させて印字を行うインクジェット記録方法であって、インク組成物として請求項5～10のいずれか一項に記載の水性インク組成物を用いる、インクジェット記録方法。

【請求項13】請求項11または12に記載の記録方法によって記録が行われた、記録物。

【発明の詳細な説明】

【0001】

【発明の背景】 発明の分野

本発明は、表面改質したカーボンブラックを含んでなる水性顔料分散液、およびこの水性顔料分散液を含んでなる水性インク組成物に関する。

【0002】 背景技術

従来水性の筆記具やインクジェットプリンターに用いる記録液には、水溶性の染料が用いられてきた。一方で、近年、記録物の画質や耐久性を向上するためにカーボンブラックのような顔料が着色剤に用いられている。例えば、特開昭64-6074号および特開昭64-31881号公報には、カーボンブラックを界面活性剤や高分子分散剤で分散した水性顔料インクが記載されている。

【0003】しかしながら、これらのインクでは、記録物の印字濃度を上げるために着色剤のインク含有量を増やすと、それにともないインク粘度も急激に増加してしまうことがあった。またカーボンブラックをインク中に安定的に分散させるためには、過剰の界面活性剤または高分子分散剤が必要であるが、これらの存在は気泡発生や消泡性低下の原因となるため、特にインクジェット記録用インクの場合には、印字安定性が悪化することが観察された。

【0004】これらの課題を解決するために、特開平8-3498号および特開平10-120958号公報には、カーボンブラックに一定量以上の表面活性水素あるいはその塩を導入して、界面活性剤や高分子分散剤が無くてもカーボンブラック単独で水系溶媒に分散させることができる、表面改質カーボンブラック分散液が記載されている。また、特開平10-110127号公報には、カーボンブラックにスルホン基を導入する方法が記載されている。さらに、特開平10-95941号公報には上述の表面改質カーボンブラックとグリコールエーテル類を含むインクジェットインクが提案されている。

【0005】

【発明の概要】本発明者等は、今般、特定の範囲の比表面積/DBP吸油量比を持つ、表面を改質することにより得られた表面改質カーボンブラックによって、印字濃度の高い印刷を実現可能であり、より高画質の記録物を形成可能なインク組成物が得られるとの知見を得た。本発明は、かかる知見に基づくものである。

【0006】よって、本発明は、印字濃度の高い印刷をすることができ、より高画質の記録物を形成することができる水性顔料分散液および水性インク組成物の提供をその目的とする。

【0007】そして、本発明の水性顔料分散液は、水と、表面改質カーボンブラックとを少なくとも含んでなる水性顔料分散液であって、該表面改質カーボンブラッ

(3)

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クが、比表面積 (m^2/g) / DBP吸油量 ($\text{ml}/100\text{g}$) の比が0.3~2.5であって、かつ、親水性官能基がその表面に導入され、その結果、分散剤無しに水に分散および/または溶解が可能とされたものである。

【0008】また、本発明の水性インク組成物は、前記水性顔料分散液を少なくとも含んでなるものである。

【0009】

【発明の具体的説明】 水性顔料分散液

本発明による水性顔料分散液は、水と、表面改質カーボンブラックとを少なくとも含んでなり、この表面改質カーボンブラックは、比表面積/DBP吸油量の比が0.3~2.5のカーボンブラックであって、親水性官能基を導入することによってその表面が改質され、その結果、分散剤無しに水に分散および/または溶解が可能とされたものである。

【0010】本発明においては、カーボンブラックに親水性官能基を大量に導入することによって、カーボンブラック表面を改質し、それによって、カーボンブラック自身に親水性を保持させる。このため、表面改質されたカーボンブラックは、あたかも水溶性染料が水に単分子で溶解するように、該カーボンブラックが分散可能な粒子径 (好ましくは最小粒子径) となって分散剤の助けなしに水中に分散すると考えられる。このような表面改質カーボンブラックは、通常自己分散型カーボンブラックと言われるが、本発明においては、このようなカーボンブラックを使用する。

【0011】本発明による水性顔料分散液を用いることによって、分散剤なしにインク組成物を調製することができる。その結果、カーボンブラックの濃度を上げてもインク組成物の粘度は大きく変化することなく、高濃度のカーボンブラックをインク組成物中に存在させることができる。よって、高濃度の印刷画像が実現できる。さらに、本発明による水性顔料分散液は、特定の比表面積/DBP吸油量の比である、特定の表面改質がなされたカーボンブラックを用いることで、本発明による要件を満足しないカーボンブラックと比較して、顕著な画像の改善が図られるとの利点を有する。

【0012】本発明において、「分散剤なしに水に分散および/または溶解」とは、カーボンブラックが分散剤を用いることなく水中に分散可能な粒子径で安定的に存在している状態を意味する。分散可能な粒子径とは、分散時間を増してもそれ以上粒子が小さくならない粒子径をいう。

【0013】本発明において、表面改質するために使用されるカーボンブラックは、比表面積 (m^2/g) とDBP吸油量 ($\text{ml}/100\text{g}$) の比が0.3~2.5のカーボンブラックであり、比表面積/DBP吸油量の比が0.3~1.75のカーボンブラックが好ましい。

【0014】本発明において、比表面積 (m^2/g)

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は、カーボンブラックにガスを吸着させ、その吸着量と吸着状態における分子断面積からカーボンブラックの表面積を算出すること (窒素吸着法として知られている) によって求めることができる。なお、本発明において、カーボンブラックの比表面積という場合には、表面改質カーボンブラック、およびその原料とされる表面未改質のカーボンブラックのいずれの態様のカーボンブラックに基づく比表面積も包含されるものとする。また、表面改質カーボンブラックの比表面積と、表面未改質のカーボンブラックの比表面積とは、実質的に同じであり、ほぼ同等の値を示すと推定される。

【0015】また、DBP吸油量 ($\text{ml}/100\text{g}$) は、カーボンブラック100gにより吸収されるフタル酸ジブチル (DBP) 量として表される値であり、JIS K6221に規定されている測定法にしたがって求めることができる。なお、前記測定法によれば、アブソーブメーターを使用し、カーボンブラックにDBPを添加した時の最大トルクの70%から求めた100g当たりのDBP吸収量が求められる。

【0016】本発明において好ましく用いられるカーボンブラックの具体例としては、三菱化学株式会社製のカーボンブラックである、#20Bおよび#40等；デグサ社製のカーボンブラックである、カラーブラックFW18、カラーブラックS170、およびスペシャルブラック250等；コロソビアカーボン社製のカーボンブラックである、コンダクテックスSC、およびラーベン1255等；および、キャボット社製のカーボンブラックである、モナーク700、モナーク880、およびエルフテックス12等が挙げられる。

【0017】本発明における表面改質カーボンブラックは、前記のようなカーボンブラックに、親水性官能基を導入して表面を改質することによって得ることができる。

【0018】ここで、「親水性官能基を導入する」とは、カルボキシル基、カルボニル基、ヒドロキシル基、スルホン基、燐酸基、および第4級アンモニウム塩等の親水性官能基、およびその塩を、顔料であるカーボンブラックの表面に、直接またはアルキル基、アルキルエーテル基、もしくはアリール基などを介して、結合することを意味する。

【0019】例えば、本発明における表面改質カーボンブラックは、真空プラズマ等の物理的处理や化学的处理により、官能基または官能基を含んだ活性種を顔料表面にグラフトさせることによって得ることができる。また、該表面改質カーボンブラックは、水中で顔料表面を酸化剤で酸化してカルボキシル基やスルホン基等の親水性官能基を導入することによって、またはp-アミノ安息香酸等を結合することによってフェニル基を介してカルボキシル基を導入することによっても得られる。

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【0020】本発明の好ましい態様においては、表面改質カーボンブラックは、水中で顔料のカーボンブラック表面を酸化剤で酸化して該表面に親水性官能基が導入されてなるものである。

【0021】本発明のさらに好ましい態様においては、表面改質カーボンブラックは、比表面積/DBP吸油量の比が0.3~2.5であって、次亜ハロゲン酸またはその塩を用いて湿式酸化して親水性官能基がその表面に導入されてなるものである。ここで、次亜ハロゲン酸またはその塩としては、例えば、次亜塩素酸水溶液、次亜塩素酸ナトリウム、次亜塩素酸カリウム、次亜臭素酸水溶液、次亜臭素酸ナトリウム、および次亜臭素酸カリウムなどが挙げられる。これらの中では、反応性やコストの点から、次亜塩素酸ナトリウムが好ましい。

【0022】したがって、本発明によれば、前記した水性顔料分散液の製造方法であって、比表面積/DBP吸油量の比が0.3~2.5であるカーボンブラックを、次亜ハロゲン酸またはその塩を用いて湿式酸化して親水性官能基を導入し、分散剤無しに前記カーボンブラックを水に分散および/または溶解させる工程を含んでなる方法も提供される。

【0023】水中で顔料表面を酸化して親水性官能基を導入して表面改質カーボンブラックを得るためには、通常、上述のようなカーボンブラックと例えば次亜塩素酸ナトリウムとを水中において混合して、5時間以上、好ましくは10~20時間、反応を進行させる。その際、カーボンブラックは、反応させる前に粉砕しておくか、または粉砕しながら同時に反応させることが好ましい。粉砕方法としては、ガラス、ジルコニア、アルミナ、ステンレス、もしくは磁性などのビーズと共に、カーボンブラックを、ボールミル、アトライター、コロイドミルもしくはサンドミルなどによって粉砕することによって行ってもよい。また、カーボンブラックが解砕され易いものである場合には、回転式ホモジナイザーまたは超音波ホモジナイザーによってカーボンブラックの粉砕を行ってもよい。

【0024】カーボンブラックを粉砕および酸化した後、得られた液からビーズと粗大粒子を分離して取り除き、次いで、酸化剤の副生成物や過剰のイオンを除くための限外ろ過等の精製を行って、水性顔料分散液が得られる。また必要に応じて、分離膜等での濃縮、金属フィルターやメンブランフィルターなどを用いた濾過、または遠心分離による分級等を行ってもよく、また、アルカリ金属塩の水酸化物もしくはアミンによって中和を行ってもよい。

【0025】本発明による水性顔料分散液においては、湿式酸化した後の表面改質カーボンブラックにおける親水性官能基量は、好ましくは1.5mmol/g以上である。親水性官能基量がこのような値であることにより、分散剤無しに水に分散または溶解することが可能とな

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る。酸化処理で生成した表面改質カーボンブラックにおけるカルボキシル基、カルボニル基もしくはヒドロキシル基などの親水性官能基量は、一般的なカーボンブラックの揮発分を測定する真空熱分解ガス法により判定することができる。なお、前記真空熱分解ガス法とは、日本化学会誌第88巻3号(1967年)第69~74頁に記載の方法であって、具体的には次のような方法である。

【0026】すなわち、表面改質カーボンブラックにおける親水性官能基量は、図1のような、電気炉とガスクロマトグラフとを備えてなる真空熱分析装置を使用することにより測定される。ここで、ガスクロマトグラフは中間セル式のものとし、カラムは一段目にシリカゲル、二段目にモレキュラーシーブ13Xをそれぞれ充填し、アルゴンをキャリアーガスとして使用する。試料であるカーボンブラック0.1~0.5gを秤量して石英管に入れ、電気炉に装填し、前処理として吸着水分や空気を除去するため120℃で2時間真空排気する。次に電気炉の温度調節計を200℃に設定して1時間保ち、その間の発生ガスを捕集し、ガスクロマトグラフにかけて組成を分析する。そしてただちに、300℃に設定してつづく1時間の発生ガスを捕集して分析し、以後、順次、400℃、500℃、600℃、700℃、800℃、900℃および1000℃における各1時間の発生ガスを捕集し、その組成を分析する。なお、発生ガスは主として一酸化炭素および二酸化炭素である。このようにして得られた各温度条件における発生ガス中の組成のデータから、表面改質カーボンブラックにおける親水性官能基量を算出する。

【0027】本発明による水性顔料分散液においては、水が主溶媒である。水は、イオン交換水、限外濾過水、逆浸透水、蒸留水等の純水、または超純水を用いることができる。また、紫外線照射、または過酸化水素添加などにより滅菌した水を用いることにより、水性顔料分散液を長期保存する場合にカビやバクテリアの発生を防止することができるので好適である。

【0028】インク組成物

本発明による水性インク組成物は、インク組成物を用いた記録方式に用いられる。インク組成物を用いた記録方式とは、例えば、インクジェット記録方式、ペン等による筆記具による記録方式、その他各種の印字方式が挙げられる。したがって、本発明による水性インク組成物は、例えば水性ペンなどの筆記具類、インクジェット記録方法、印刷、スタンプなどの用途に好ましく用いることができる。

【0029】本発明による水性インク組成物は、前記した水性顔料分散液を少なくとも含んでなるものである。

【0030】本発明による水性インク組成物は、表面改質カーボンブラックを、インク組成物に対して、好ましくは1~15重量%の範囲で含有し、より好ましくは2

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～10重量%の範囲で含有する。このような範囲でインク組成物が表面改質カーボンブラックを含有することは、充分な印字濃度を確保しつつ、インクジェット記録方式で使用可能な粘度のインク組成物を得ることができる点で有利である。

【0031】本発明による水性インク組成物は、水を主溶媒とすることが好ましい。水は、イオン交換水、限外濾過水、逆浸透水、蒸留水等の純水、または超純水を用いることができる。また、紫外線照射、または過酸化水素添加などにより滅菌した水を用いることにより、水性インク組成物を長期保存する場合にカビやバクテリアの発生を防止することができるので好適である。

【0032】本発明の好ましい態様においては、水性インク組成物は、前記した水性顔料分散液を含んでなるものであって、記録媒体へのインク組成物の塗布量が 1 mg/cm^2 であるとき、インク組成物の浸透時間が1秒未満であるような浸透性を有するものであることが好ましい。

【0033】ここで、塗布量が 1 mg/cm^2 であるときの浸透時間が1秒未満であるような浸透性とは、具体的には、例えば 360 dpi （ドット/インチ） $\times 360\text{ dpi}$ の面積に 50 ng のインク組成物を普通紙に塗布した場合に、印刷面を触ってもインク組成物で汚れなくなるまでの時間が1秒未満である場合をいう。このとき、普通紙としては、中性普通紙、例えばゼロックスP（商品名、富士ゼロックス株式会社製）を用いる。

【0034】このようなインク組成物の浸透性は、水溶液の表面張力を低下させる水溶性有機溶剤もしくは界面活性剤のような浸透促進剤を添加することによって、記録媒体への濡れ性を向上することにより得ることができる。

【0035】このような水溶性有機溶剤としては、例えば、エタノール、プロパノール等の低級アルコール、エチレングリコールモノメチルエーテル、エチレングリコールモノエチルエーテル等のセロソルブ類、ジエチレングリコールモノメチルエーテル、ジエチレングリコールモノエチルエーテル等のカルビトール類、および、1, 2-ヘキサジオール、1, 2-オクタジオール等の1, 2-アルキルジオール類が挙げられる。

【0036】本発明の更に好ましい態様においては、浸透促進剤として使用される水溶性有機溶剤としては、グリコールブチルエーテル系の水溶性有機溶剤がより好ましい。このようなグリコールブチルエーテル系の水溶性有機溶剤としては、例えば、エチレングリコールモノn-ブチルエーテル、ジエチレングリコールn-ブチルエーテル、およびトリエチレングリコールn-ブチルエーテル等が挙げられる。このような水溶性有機溶剤と表面改質カーボンブラックとを組み合わせることにより、印字時のにじみが低減された良好な印字物を提供することができる。

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【0037】前記のような界面活性剤としては、例えば、脂肪酸塩類、アルキル硫酸エステル塩類等のアニオン性界面活性剤、ポリオキシエチレンアルキルエーテル、ポリオキシエチレンフェニルエーテル等のノニオン性界面活性剤、カチオン性界面活性剤、および両イオン性界面活性剤等が挙げられる。

【0038】より好ましい界面活性剤としては、ポリオキシエチレンアルキルエーテル、ポリオキシエチレンフェニルエーテル等のノニオン性界面活性剤が挙げられる。これらはイオン性の界面活性剤に比較してインクの発泡を低減できる点から有利である。このようなノニオン性界面活性剤の具体例としては、ニッサンノニオンK-211、K-220、P-213、E-215、E-220、S-215、S-220、HS-220、NS-212、およびNS-220（以上いずれも商品名、日本油脂株式会社製）等が挙げられる。さらに好ましい界面活性剤の例としては、ノニオン性界面活性剤の中で、サーフィノール61、82、104、440、465、485（以上いずれも商品名、エア・プロダクツ・アンド・ケミカルズ社製）等のアセチレングリコール系界面活性剤が挙げられる。これらを、インク組成物に添加すると、発泡がほとんど生じなくなるため、インク組成物をインクジェット記録方法において使用する場合には特に好適である。

【0039】なお、本発明における表面改質カーボンブラックは、界面活性剤のような分散剤を用いること無く水に分散および/または溶解が可能なものであるため、本発明によるインク組成物において用られるこれら界面活性剤は、浸透促進効果のみを目的として選択することができる。すなわち、通常、顔料に分散性を付与するためには、顔料と各々の材料とが吸着し合う組み合わせを考慮して選ぶ必要があるが、本発明においては、そのような組み合わせを考慮することなく、浸透促進効果のみを考慮して界面活性剤を選択することができる。

【0040】本発明においては、浸透促進剤として、前記したような水溶性有機溶剤もしくは界面活性剤を単独で、またはそれらを併用して、使用することによって、インク組成物の表面張力を、 40 mN/m 未満、好ましくは 35 mN/m 未満に調整することが望ましい。

【0041】本発明による水性インク組成物は、インクジェット記録方法に用いた場合に、インクを吐出するノズルの先端のインク乾燥防止を目的として、保湿剤をさらに含んでなることができる。

【0042】このような保湿剤は、通常、水溶性かつ吸湿性の高い材料から選択される。具体的には、例えば、グリセリン、エチレングリコール、ジエチレングリコール、トリエチレングリコール、ポリエチレングリコール、プロピレングリコール、ジプロピレングリコール、ポリプロピレングリコール、1, 3-プロパンジオール、1, 4-ブタンジオール、1, 5-ペンタンジオール

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～10重量%の範囲で含有する。このような範囲でインク組成物が表面改質カーボンブラックを含有することは、充分な印字濃度を確保しつつ、インクジェット記録方式で使用可能な粘度のインク組成物を得ることができる点で有利である。

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【0032】本発明の好ましい態様においては、水性インク組成物は、前記した水性顔料分散液を含んでなるものであって、記録媒体へのインク組成物の塗布量が 1 mg/cm^2 であるとき、インク組成物の浸透時間が1秒未満であるような浸透性を有するものであることが好ましい。

【0033】ここで、塗布量が 1 mg/cm^2 であるときの浸透時間が1秒未満であるような浸透性とは、具体的には、例えば 360 dpi （ドット/インチ） $\times 360\text{ dpi}$ の面積に 50 ng のインク組成物を普通紙に塗布した場合に、印刷面を触ってもインク組成物で汚れなくなるまでの時間が1秒未満である場合をいう。このとき、普通紙としては、中性普通紙、例えばゼロックスP（商品名、富士ゼロックス株式会社製）を用いる。

【0034】このようなインク組成物の浸透性は、水溶液の表面張力を低下させる水溶性有機溶剤もしくは界面活性剤のような浸透促進剤を添加することによって、記録媒体への濡れ性を向上することにより得ることができる。

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【0037】前記のような界面活性剤としては、例えば、脂肪酸塩類、アルキル硫酸エステル塩類等のアニオン性界面活性剤、ポリオキシエチレンアルキルエーテル、ポリオキシエチレンフェニルエーテル等のノニオン性界面活性剤、カチオン性界面活性剤、および両イオン性界面活性剤等が挙げられる。

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【0039】なお、本発明における表面改質カーボンブラックは、界面活性剤のような分散剤を用いること無く水に分散および/または溶解が可能なものであるため、本発明によるインク組成物において用られるこれら界面活性剤は、浸透促進効果のみを目的として選択することができる。すなわち、通常、顔料に分散性を付与するためには、顔料と各々の材料とが吸着し合う組み合わせを考慮して選ぶ必要があるが、本発明においては、そのような組み合わせを考慮することなく、浸透促進効果のみを考慮して界面活性剤を選択することができる。

【0040】本発明においては、浸透促進剤として、前記したような水溶性有機溶剤もしくは界面活性剤を単独で、またはそれらを併用して、使用することによって、インク組成物の表面張力を、 40 mN/m 未満、好ましくは 35 mN/m 未満に調整することが望ましい。

【0041】本発明による水性インク組成物は、インクジェット記録方法に用いた場合に、インクを吐出するノズルの先端のインク乾燥防止を目的として、保湿剤をさらに含んでなることができる。

【0042】このような保湿剤は、通常、水溶性かつ吸湿性の高い材料から選択される。具体的には、例えば、グリセリン、エチレングリコール、ジエチレングリコール、トリエチレングリコール、ポリエチレングリコール、プロピレングリコール、ジプロピレングリコール、ポリプロピレングリコール、1, 3-プロパンジオール、1, 4-ブタンジオール、1, 5-ペンタンジオール、

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ル、1, 6-ヘキサンジオール、1, 2, 6-ヘキサントリオール、ペンタエリスリトール等のポリオール類、2-ピロリドン、N-メチル-2-ピロリドン、ε-カプロラクタム等のラクタム類、尿素、チオ尿素、エチレン尿素、1, 3-ジメチルイミダゾリジノン類等の尿素類、マルチトール、ソルビトール、グルコノラクトン、マルトース等の糖類が挙げられる。

【0043】これらの保湿剤は、他のインク添加剤と併用することによって、インク組成物の粘度を25℃で25 mPa・s 以下になるような量で本発明によるインク組成物に添加することができる。

【0044】本発明による水性インク組成物には、必要に応じて、定着剤、pH調整剤、酸化防止剤、紫外線吸収剤、防腐剤および防かび剤等をさらに添加することができる。

【0045】定着剤としては、水溶性の樹脂類を用いることができる。そのような定着剤としては、例えば、水溶性ロジン類、アルギン酸類、ポリビニルアルコール、ヒドロキシプロピルセルロース、カルボキシメチルセルロース、ヒドロキシエチルセルロース、メチルセルロース、スチレン-アクリル酸樹脂、スチレン-アクリル酸-アクリル酸エステル樹脂、スチレン-マレイン酸樹脂、スチレン-マレイン酸半エステル樹脂、アクリル酸-アクリル酸エステル樹脂、イソブチレン-マレイン酸樹脂、ロジン変性マレイン酸樹脂、ポリビニルピロリドン、アラビアゴムスターチ、ポリアリルアミン、ポリビニルアミン、ポリエチレンイミンなどが挙げられる。なお、本発明の表面改質カーボンブラックは、水溶性樹脂からなる分散剤を用いることなく水に分散および/または溶解が可能な着色剤であるため、本発明のインクで用いる水溶性樹脂は、定着効果のみを目的として選択することができる。すなわち、通常顔料に分散性を付与するためには顔料と各々の材料が吸着し合う組み合わせで選ぶ必要があるが、本発明では、組み合わせを考慮せずに定着性のみを考慮して選択することができる。

【0046】pH調整剤としては、例えば、水酸化リチウム、水酸化ナトリウム、水酸化カリウム、トリエタノールアミン、ジエタノールアミンなどのアルカリ金属の水酸化物あるいはアミン類が挙げられる。

【0047】酸化防止剤および紫外線吸収剤としては、例えば、アロハネート、メチルアロハネートなどのアロハネート類、ビウレット、ジメチルビウレット、テトラメチルビウレットなどのビウレット類など、L-アスコルビン酸およびその塩等、チバガイギー社製のTinuvin 328、900、1130、384、292、123、144、622、770、292、Irgacor 252、153、Irganox 1010、1076、1035、MD1024、またはランタニドの酸化物等が挙げられる。

【0048】防腐剤および防かび剤としては、例えば、

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安息香酸ナトリウム、ペンタクロロフェノールナトリウム、2-ピリジンチオール-1-オキサイドナトリウム、ソルビン酸ナトリウム、デヒドロ酢酸ナトリウム、1, 2-ジベンジソチアゾリン-3-オン（ICI社のプロキセルCRL、プロキセルBDN、プロキセルGXL、プロキセルXL-2、プロキセルTN）などが挙げられる。

【0049】記録方法

本発明によるインク組成物は、インク組成物を付着させて記録媒体に印字を行う記録方式に用いられる。

【0050】本発明の別の態様によれば、本発明によるインク組成物の液滴を吐出し記録媒体に付着させて印字を行うインクジェット記録方法が提供される。本発明によるインクジェット記録方法としては、インク組成物を微細なノズルより液滴として吐出して、その液滴を記録媒体に付着させる方法であればいかなる方法も使用することができる。そのような方法の具体例としては、種々の態様の方法が知られている。

【0051】そのような方法の一例としては、例えば、静電吸引方式が挙げられる。この方式では、ノズルとノズルの前方に置いた加速電極の間に強電界を印可し、ノズルからインクを液滴状で連続的に噴射させ、インク滴が偏向電極間を飛翔する間に印刷情報信号を偏向電極に与えて記録する。また、この方法においては必要に応じて、インク滴を偏向させることなく印刷情報信号に対応して噴射させてもよい。他の態様としては、小型ポンプでインク液に圧力を加え、ノズルを水晶振動子等で機械的に振動させることにより、強制的にインク滴を噴射させる方法がある。この方法では、噴射したインク滴は噴射と同時に帯電させ、インク滴が偏向電極間を飛翔する間に印刷情報信号を偏向電極に与えて記録する。別の態様としては、圧電素子を用いる方法が挙げられる。この方法では、インク液に圧電素子で圧力と印刷情報信号を同時に加え、インク滴を噴射させ、記録を行う。さらに別の態様としては、熱エネルギーの作用によりインク液を急激に体積膨張させる方法がある。この方法では、インク液を印刷情報信号に従って微小電極で加熱発泡させ、インク滴を噴射させ、記録を行う。本発明によるインクジェット記録方法によれば、安定的にインクジェット記録を行うことができる。

【0052】さらに本発明によれば、これらの記録方法により記録された記録物も提供される。

【0053】

【実施例】以下本発明を以下の実施例によって詳細に説明するが、本発明はこれらに限定されるものではない。

【0054】顔料分散液の調整 顔料分散液1

比表面積/DBP吸油量の比率が1.63のカーボンブラックのカラーブラックFW18（商品名、デグサ社

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製) 35 g を水 1 k g に混合して、ジルコニアビーズによるボールミルにて粉碎した。この粉碎原液に次亜塩素酸ナトリウム 500 g を加えて、10 時間煮沸して湿式酸化を行った。得られた分散原液をガラス繊維ろ紙 GA-100 (商品名、アドバンテック東洋株式会社製) でろ過して、さらに水で洗浄した。得られたウェットケーキを水 5 k g に再分散して、逆浸透膜により電導度が 2 mS/cm になるまで脱塩および精製し、さらに顔料濃度が 10 重量% になるまで濃縮して、顔料分散液 1 を調整した。

【0055】顔料分散液 2

比表面積/DBP 吸油量の比率が 1.33 のカーボンブラックのカラーブラック S170 (商品名、デグサ社製) 40 g を水 1 k g に混合して、ジルコニアビーズによるボールミルにて粉碎した。この粉碎原液に次亜塩素酸ナトリウム 500 g を加えて、ボールミルで粉碎しながら 5 時間反応させ、さらに攪拌しながら 4 時間煮沸して湿式酸化を行った。得られた分散原液をガラス繊維ろ紙 GA-100 (商品名、アドバンテック東洋株式会社製) でろ過して、さらに水で洗浄した。得られたウェットケーキを水 5 k g に再分散して、逆浸透膜により電導度が 2 mS/cm になるまで脱塩および精製し、さらに顔料濃度が 10 重量% になるまで濃縮して、顔料分散液 2 を調整した。

【0056】顔料分散液 3

比表面積/DBP 吸油量の比率が 1.91 のカーボンブラックのコンダクテックス SC (商品名、コロンビアカーボン社製) 40 g を水 1 k g に混合して、ジルコニアビーズによるボールミルにて粉碎した。この粉碎原液に次亜塩素酸ナトリウム 500 g を加えて、10 時間煮沸して湿式酸化を行った。得られた分散原液をガラス繊維ろ紙 GA-100 (商品名、アドバンテック東洋株式会社製) でろ過して、さらに水で洗浄した。得られたウェットケーキを水 5 k g に再分散して、逆浸透膜により電導度が 2 mS/cm になるまで脱塩および精製し、さらに顔料濃度が 10 重量% になるまで濃縮して、顔料分散液 3 を調整した。

【0057】顔料分散液 4

比表面積/DBP 吸油量の比率が 1.14 のカーボンブラックの #40 (商品名、三菱化学株式会社製) 60 g を水 1 k g に混合して、ジルコニアビーズによるボールミルにて粉碎した。この粉碎原液に次亜塩素酸ナトリウム 500 g を加えて、ボールミルで粉碎しながら 5 時間反応させ、さらに攪拌しながら 4 時間煮沸して湿式酸化を行った。得られた分散原液をガラス繊維ろ紙 GA-100 (商品名、アドバンテック東洋株式会社製) でろ過して、さらに水で洗浄した。得られたウェットケーキを水 5 k g に再分散して、逆浸透膜により電導度が 2 mS/cm になるまで脱塩および精製し、さらに顔料濃度が 10 重量% になるまで濃縮して、顔料分散液 4 を調整し

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た。

【0058】顔料分散液 5

比表面積/DBP 吸油量の比率が 1.91 のカーボンブラックのコンダクテックス SC (商品名、コロンビアカーボン社製) 40 g を水 1 k g に混合して、ジルコニアビーズによるボールミルにて粉碎した。この粉碎原液に次亜塩素酸ナトリウム 500 g を加えて、10 時間煮沸して湿式酸化を行った。得られた分散原液をガラス繊維ろ紙 GA-100 (商品名、アドバンテック東洋株式会社製) でろ過して、さらに水で洗浄した。得られたウェットケーキを水 5 k g に再分散して、逆浸透膜により電導度が 2 mS/cm になるまで脱塩および精製し、さらに顔料濃度が 15 重量% になるまで濃縮して、顔料分散液 5 を調整した。

【0059】顔料分散液 6

比表面積/DBP 吸油量の比率が 1.97 のカーボンブラックのラーベン 1255 (商品名、コロンビアカーボン社製) 100 g を N-メチルピロリドン 5 k g に混合して、ジルコニアビーズによるボールミルにて粉碎した。この粉碎原液にスルファミン酸 50 g を加えて、10 時間 150℃ でスルホン化した。全量を氷 10 k g に投入して、分散原液をガラス繊維ろ紙 GA-100 (商品名、アドバンテック東洋株式会社製) でろ過して、さらに水 5 k g に再分散して、ろ過および洗浄した。得られたウェットケーキを水 2 k g に再分散して、逆浸透膜により電導度が 2 mS/cm になるまで脱塩および精製し、さらに顔料濃度が 15 重量% になるまで濃縮して、顔料分散液 6 を調整した。

【0060】顔料分散液 7

比表面積/DBP 吸油量の比率が 1.63 のカーボンブラックのカラーブラック FW18 (商品名、デグサ社製) 35 g を水 1 k g に混合して、ジルコニアビーズによるボールミルにて粉碎した。この粉碎原液に次亜塩素酸ナトリウム 500 g を加えて、10 時間煮沸して湿式酸化を行った。得られた分散原液をガラス繊維ろ紙 GA-100 (商品名、アドバンテック東洋株式会社製) でろ過して、さらに水で洗浄した。得られたウェットケーキを水 5 k g に再分散して、逆浸透膜により電導度が 2 mS/cm になるまで脱塩および精製し、さらに顔料濃度が 15 重量% になるまで濃縮して、顔料分散液 7 を調整した。

【0061】顔料分散液 8

比表面積/DBP 吸油量の比率が 1.33 のカーボンブラックのカラーブラック S170 (商品名、デグサ社製) 40 g を水 1 k g に混合して、ジルコニアビーズによるボールミルにて粉碎した。この粉碎原液に次亜塩素酸ナトリウム 500 g を加えて、ボールミルで粉碎しながら 5 時間反応させ、さらに攪拌しながら 4 時間煮沸して湿式酸化を行った。得られた分散原液をガラス繊維ろ紙 GA-100 (商品名、アドバンテック東洋株式会社

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製)でろ過して、さらに水で洗浄した。得られたウェットケーキを水5kgに再分散して、逆浸透膜により電導度が2mS/cmになるまで脱塩および精製し、さらに顔料濃度が15重量%になるまで濃縮して、顔料分散液8を調整した。

【0062】顔料分散液9 (比較例)

比表面積/DBP吸油量の比率が2.56のカーボンブラックの#45L (商品名、三菱化学株式会社製) 100gを水1kgに混合して、ジルコニアビーズによるボールミルにて粉碎した。この粉碎原液に次亜塩素酸ナトリウム500gを加えて、ボールミルで粉碎しながら5時間反応させ、さらに攪拌しながら4時間煮沸して湿式酸化を行った。得られた分散原液をガラス繊維ろ紙GA-100 (商品名、アドバンテック東洋株式会社製)でろ過して、さらに水で洗浄した。得られたウェットケーキを水5kgに再分散して、逆浸透膜により電導度が2mS/cmになるまで脱塩および精製し、さらに顔料濃度が10重量%になるまで濃縮して、顔料分散液9を調整した。

【0063】顔料分散液10 (比較例)

比表面積/DBP吸油量の比率が0.24のカーボンブラックのラーベン16 (商品名、コロンビアカーボン社製) 300gを水1kgに混合して、ジルコニアビーズによるボールミルにて粉碎した。この粉碎原液に次亜塩素酸ナトリウム300gを加えて、ボールミルで粉碎しながら5時間反応させ、さらに攪拌しながら4時間煮沸して湿式酸化を行った。得られた分散原液をガラス繊維ろ紙GA-100 (商品名、アドバンテック東洋株式会社製)でろ過して、さらに水で洗浄した。得られたウェットケーキを水5kgに再分散して、逆浸透膜により電導度が2mS/cmになるまで脱塩および精製し、さらに顔料濃度が10重量%になるまで濃縮して、顔料分散液10を調整した。

【0064】顔料分散液11 (比較例)

実施例1で用いたカラーブラックFW18 (商品名、デグサ社製) 100g、水溶性樹脂の分散剤のジョンクリルJ-62 (商品名、ジョンソンポリマー社製) 150g、水酸化ナトリウム6g、水250gを混合して、ジルコニアビーズによるボールミルにて10時間分散を行った。得られた分散原液を孔径約5μmのステンレス製フィルターにより濾過して、水で顔料濃度が10重量%になるまで希釈して、水溶性樹脂で分散した顔料分散液11を調整した。

【0065】インク組成物の調整

インク組成物1

作成した水性顔料分散液 (顔料分散液1) 20g、保湿成分としてグリセリン5gと2-ピロリドン5g、浸透促進成分としてエタノール4gを混合して、全量が100gまで超純水を加えた。この混合液を2時間攪拌して、孔径約5μmのステンレス製フィルターにて濾過し

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てインク組成物1を調製した。

【0066】インク組成物2

作成した水性顔料分散液 (顔料分散液2) 20g、保湿成分としてトリエチレングリコール6gと尿素5g、浸透促進成分としてエタノール4gを混合して、全量が100gまで超純水を加えた。この混合液を2時間攪拌して、孔径約5μmのステンレス製フィルターにて濾過してインク組成物2を調製した。

【0067】インク組成物3

10 顔料分散液5を45g、保湿成分としてグリセリン10gと2-ピロリドン5g、浸透促進成分としてtert-ペンタノール4gとノニオン性界面活性剤のニッサンノニオンNS-220 (商品名、日本油脂株式会社製) 1gを混合して、超純水を加えて全量を100gとして、さらにインクpHが7.5になるまでトリエタノールアミンを加えた。この混合液を2時間攪拌して、孔径約5μmのステンレス製フィルターにて濾過してインク組成物3を調製した。

【0068】インク組成物4

20 顔料分散液6を45g、保湿剤としてトリエチレングリコール10gとジエチレングリコール5g、浸透促進剤としてノニオン性界面活性剤のニッサンノニオンNS-210 (商品名、日本油脂株式会社製) 2.5gを混合して、超純水を加えて全量を100gとして、さらにインクpHが7.5になるまでトリエタノールアミンを加えた。この混合液を2時間攪拌して、孔径約5μmのステンレス製フィルターにて濾過してインク組成物4を調製した。

【0069】インク組成物5

30 顔料分散液7を45g、保湿成分としてグリセリン10gと2-ピロリドン5g、浸透促進成分としてtert-ペンタノール4gとノニオン性界面活性剤のニッサンノニオンNS-220 (商品名、日本油脂株式会社製) 1gを混合して、超純水を加えて全量を100gとして、さらにインクpHが7.5になるまでトリエタノールアミンを加えた。この混合液を2時間攪拌して、孔径約5μmのステンレス製フィルターにて濾過してインク組成物5を調製した。

【0070】インク組成物6

40 顔料分散液8を45g、保湿剤としてトリエチレングリコール10gとジエチレングリコール5g、浸透促進剤としてノニオン性界面活性剤のニッサンノニオンNS-210 (商品名、日本油脂株式会社製) 2.5gを混合して、超純水を加えて全量を100gとして、さらにインクpHが7.5になるまでトリエタノールアミンを加えた。この混合液を2時間攪拌して、孔径約5μmのステンレス製フィルターにて濾過してインク組成物6を調製した。

【0071】インク組成物7

50 顔料分散液8を45g、保湿剤としてグリセリン10g

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とジエチレングリコール5g、浸透促進剤としてジエチレングリコールモノ-n-ブチルエーテル7.5gを混合して、超純水を加えて全量を100gとして、さらにインクpHが7.3になるまでトリエタノールアミンを加えた。この混合液を2時間攪拌して、孔径約5 μ mのステンレス製フィルターにて濾過してインク組成物7を調製した。

【0072】インク組成物8

顔料分散液7を45g、保湿剤としてグリセリン10gと1,5-ペンタンジオール5g、浸透促進剤としてトリエチレングリコールモノ-n-ブチルエーテル5gを混合して、超純水を加えて全量を100gとして、さらにインクpHが7.3になるまでトリエタノールアミンを加えた。この混合液を2時間攪拌して、孔径約5 μ mのステンレス製フィルターにて濾過してインク組成物8を調製した。

【0073】インク組成物9

顔料分散液7を45g、保湿剤としてグリセリン7.5gと1,5-ペンタンジオール7.5g、浸透促進剤としてアセチレングリコール系界面活性剤のサーフィノール104を0.3gとサーフィノール485を1.5gを混合して、超純水を加えて全量を100gとして、さらにインクpHが7.3になるまでトリエタノールアミンを加えた。この混合液を2時間攪拌して、孔径約5 μ mのステンレス製フィルターにて濾過してインク組成物9を調製した。

【0074】インク組成物10

顔料分散液8を45g、保湿剤としてグリセリン10gとジエチレングリコール5g、浸透促進剤としてジエチレングリコールモノ-n-ブチルエーテル5gとアセチレングリコール系界面活性剤のサーフィノール465を1gを混合して、超純水を加えて全量を100gとして、さらにインクpHが7.2になるまでトリエタノールアミンを加えた。この混合液を2時間攪拌して、孔径約5 μ mのステンレス製フィルターにて濾過してインク組成物10を調製した。

【0075】インク組成物11（比較例）

顔料分散液9を用いる以外はインク組成物1の場合と同様の方法でインク組成物11を調製した。

【0076】インク組成物12（比較例）

顔料分散液10を用いる以外はインク組成物1の場合と同様の方法でインク組成物12を調製した。

*【0077】インク組成物13（比較例）

顔料分散液11を用いる以外はインク組成物1の場合と同様の方法でインク組成物13を調製した。

【0078】インク組成物14（比較例）

比表面積/DBP吸油量の比率が2.56のカーボンブラックの#45L（商品名、三菱化学株式会社製）300gを水1kgに混合して、ジルコニアビーズによるボールミルにて粉碎した。この粉碎原液に次亜塩素酸ナトリウム450gを加えて、ボールミルで粉碎しながら5時間反応させ、さらに攪拌しながら4時間煮沸して湿式酸化を行った。得られた分散原液をガラス繊維ろ紙GA-100（商品名、アドバンテック東洋株式会社製）でろ過して、さらに水で洗浄した。得られたウェットケーキを水5kgに再分散して、逆浸透膜により電導度が2mS/cmになるまで脱塩および精製し、さらに顔料濃度が15重量%になるまで濃縮して顔料分散液を調整した。この顔料分散液45gを用いてインク組成物7の場合と同様にしてインク組成物14を作成した。

【0079】インク組成物15（比較例）

比表面積/DBP吸油量の比率が0.24のカーボンブラックのラーベン16（商品名、コロンビアカーボン社製）300gを水1kgに混合して、ジルコニアビーズによるボールミルにて粉碎した。この粉碎原液に次亜塩素酸ナトリウム300gを加えて、ボールミルで粉碎しながら5時間反応させ、さらに攪拌しながら4時間煮沸して湿式酸化を行った。得られた分散原液をガラス繊維ろ紙GA-100（商品名、アドバンテック東洋株式会社製）でろ過して、さらに水で洗浄した。得られたウェットケーキを水5kgに再分散して、逆浸透膜により電導度が2mS/cmになるまで脱塩および精製し、さらに顔料濃度が15重量%になるまで濃縮して顔料分散液を調整した。この顔料分散液45gを用いてインク組成物7の場合と同様にしてインク組成物15を作成した。

【0080】顔料分散液の評価

顔料分散液1～4および顔料分散液9～11のそれぞれを塗布厚み25 μ mのアプリケータにより中性普通紙のゼロックスP（商品名、富士ゼロックス株式会社製）に塗布して乾燥させ、マクベス濃度計TR-927（商品名、コルモーゲン社製）を用いて各OD値を測定した。結果は表1に示される通りであった。

【0081】

表1

顔料分散液	比表面積/DBP吸油量の比	OD値
1	1.63	1.53
2	1.33	1.55
3	1.91	1.45
4	1.14	1.47
9	2.56	1.30
10	0.24	1.25

*

(10)

17

18

1 1

1. 6 3

1. 3 2

インク組成物の評価1

インク組成物1および2ならびにインク組成物11～13のそれぞれについて、圧電素子式オンデマンド型インクジェット記録装置MJ-500（商品名、セイコーエプソン株式会社製）によって中性普通紙のゼロックス*

* P（商品名、富士ゼロックス株式会社製）に印刷を行い、乾燥後、マクベス濃度計TR-927（商品名、コルモーゲン社製）により各OD値を測定した。結果は表2に示される通りであった。

【0082】

表2

インク組成物	比表面積/DBP吸油量の比	OD値
1	1. 5 3	1. 5 5
2	1. 3 3	1. 5 5
11	2. 5 6	1. 3 1
12	0. 2 4	1. 3 3
13	1. 6 3	1. 3 8

インク組成物の評価2

インクの浸透時間が1秒未満である浸透性を有するインク組成物3～10ならびにインク組成物14および15のそれぞれについて、圧電素子式オンデマンド型インクジェット記録装置MJ-930C（商品名、セイコーエプソン株式会社製）によって中性普通紙のゼロックス*

* P（商品名、富士ゼロックス株式会社製）に印刷を行い、乾燥後、マクベス濃度計TR-927（商品名、コルモーゲン社製）を用いて各OD値を測定した。結果は表3に示される通りであった。

【0083】

表3

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インク組成物	比表面積/DBP吸油量の比	OD値
3	1. 9 1	1. 4 0
4	1. 9 7	1. 3 7
5	1. 6 3	1. 4 2
6	1. 3 3	1. 4 4
7	1. 3 3	1. 4 4
8	1. 6 3	1. 4 2
9	1. 6 3	1. 4 3
10	1. 3 3	1. 4 7
14	2. 5 6	1. 1 7
15	0. 2 4	1. 2 4

インク組成物の評価3

前記評価2で得られた各印字物について、その印字品質（例えば、印字物のにじみ）を目視で評価した。

【0084】浸透促進剤としてグリコールブチルエーテル類を添加したインク組成物7および8の印字物は、印字の周辺部分のにじみが少なく、その印字品質は特に良好であった。

【図面の簡単な説明】

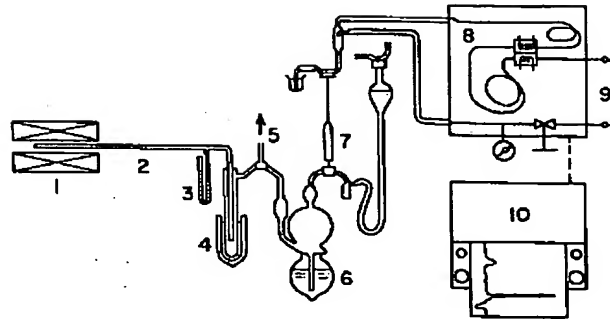
【図1】表面改質カーボンブラックにおける親水性官能基量を測定するための真空熱分解装置の概略を示す図である。

【符号の説明】

- 1 電気炉
- 2 石英試料管
- 3 マノメーター
- 4 冷却トラップ
- 5 真空ポンプ
- 6 テブラーポンプ
- 7 ガスビュレット
- 8 ガスクロマトグラフ
- 9 キャリヤーガス出入口
- 10 記録計

(11)

【図1】



フロントページの続き

(72)発明者 百 瀬 雅 之
長野県諏訪市大和三丁目3番5号 セイコーエプソン株式会社内

(72)発明者 林 広 子
長野県諏訪市大和三丁目3番5号 セイコーエプソン株式会社内

(72)発明者 伊 東 草 子
大阪府寝屋川市讃良東町8番1号 オリエン化学工業株式会社第一開発センター内